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MANUAL

OF

THE CHEMICAL ANALYSIS OF ROCKS.

BY

HENRY S. WASHINGTON, PH.D.

SECOND EDITION, REVISED AND ENLARGED

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PREFACE TO SECOND EDITION.

SINCE the publication of the first edition of this book, Hillebrand's largely rewritten and amplified "The Analysis of Silicate and Carbonate Rocks" and a small manual by Dittrich have appeared. To the first of these I am indebted for several new methods, which I have used during the past few years, and which are introduced here, as well as some other methods and modifications in practice from other sources. These supersede or supplement those advocated before. Numerous changes have been made in the text, in part because of new matter or changes in procedure and also because more detail appeared to be needed. The important work of Mauzelius, confirmed by Hillebrand, on the influence of fine grinding, is discussed. The analysis of carbonate rocks, regarded as a special subject, has not been treated, as Hillebrand's latest work covers this fully, and they are of minor importance to the petrologist.

It may be permissible to remark that since 1904 the increase in the number and, still more, the improvement in the quality, of rock analyses have been very great, as will be brought out in a subsequent work. It is hoped that this little book has done its share, along with Hillebrand's invaluable treatise, in aiding to place the science of petrology upon a firm chemical basis, the importance of which is well shown in the recent treatise on igneous rocks by Iddings. I have to record my obligations to Professor J. V. Lewis, for his kindness in undertaking to read the proofs during my absence.

LOCUST, N. J., January, 1910.

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PREFACE TO FIRST EDITION.

THE object of this book is to present to chemists, petrologists, mining engineers and others who have not made a particular study of quantitative analysis, a selection of methods for the chemical analysis of silicate rocks, and especially those of igneous origin. While the publication of such a work may seem superfluous in view of the existence of Hillebrand's treatise on this special topic, yet justification may be found in the fact that the latter is intended, not so much for one who is not very conversant with the subject, as for the practised analyst, to whom it is an indispensable guide.

A further reason for its appearance is that, apart from Hillebrand's book and a paper by Dittrich, there does not seem to exist any separate modern treatise on the chemical analysis of rocks. The space devoted to this branch of analysis in the text-books is usually very small, and the various methods are widely scattered and often inadequately described. This is especially true in regard to the minutiæ of manipulation and precautions to be observed, and to the determination of elements which, though usually accounted rare, have of late years been shown to be very common rock constituents. This neglect is rather striking in view of the prominence given in the last decade or so to the chemical composition of igneous rocks.

There is an increasing number of geologists, petrologists, chemists and others, who are desirous of making chemical analyses of rocks, but who have had little or no experience in the

subject, except that gained in the ordinary course of quantitative analysis, in which the study of silicates is usually confined to the examination of a feldspar or some such simple mineral. It is for the benefit of this class of students that the present book is written. The general plan adopted therefore is, not to attempt a complete treatise on rock analysis, but to present only certain methods which have proved simple and reliable in the experience of the chemists of the U. S. Geological Survey and of my own. The more important of these, and some of the principal operations, are described with great explicitness. Many small details of manipulation are gone into which are omitted by Hillebrand and the text-books as unnecessary, a knowledge of them being either presupposed or their demonstration left to the instructor.

In this way it is hoped that it will be possible for an intelligent student, with some knowledge of chemistry and a little analytical training, to be able to complete a satisfactory analysis of an ordinary silicate rock, without personal instruction and after comparatively short practice. To the expert analyst, therefore, the book will contain much that is superfluous, but for this no apology is offered. What are superfluities to him will, it is hoped, be welcome to the novice.

It is assumed that silicate igneous rocks will be the most frequent objects of investigation. At the same time, the methods described serve equally well for most silicate metamorphic and sedimentary rocks. Such rocks as saline deposits, coals and others containing organic matter, are not considered. The methods are not generally adapted to the analysis of ores which, with such constituents as sulphides, arsenides and other compounds of the heavy metals, often call for different and more complex means of separation than are here given. The same is true of many minerals, though the methods found in the following pages are those appropriate to the analysis of most silicates. The analysis of meteorites also demands the employment of special methods, and in most cases these bodies are of such character that their examination should not be undertaken

by the inexperienced, especially if only a limited supply of material is available.

The methods selected are, in general, those adopted by the chemists of the U. S. Geological Survey, and which in their essentials I have employed in my own scientific work for a number of years. Some modifications have been made, chiefly in the direction of simplification and the elimination of certain refinements which do not seem called for when the object of the volume is considered. There is no attempt at the introduction of new methods or the description of alternative ones which, either on theoretical grounds or on account of practical difficulties, are deemed to be less well adapted to the needs of students than those which are here given. Theoretical discussion will be limited to what may seem necessary to make clear the principles of certain methods or the reasons for their selection.

I have also endeavored to point out to the student the importance of chemical analyses for the study of rocks, and their possible bearing on some of the broad problems which form the objects of the science of petrology. In other words, it has been sought to emphasize the fact that petrographical classifications and the study of textures and of minerals in thin sections are not the sole aims of the science, but that, supplemented by a knowledge of the chemical composition of igneous rocks, they are only means to broader ends. I can only express the hope that this little book will aid in the progress of petrology, by leading to an increase in the knowledge of chemical analysis among petrologists and rendering our data in the way of rock analyses of superior quality more numerous.

The great obligations under which I am to Dr. Hillebrand's work are evident throughout and are most gratefully acknowledged. The text-books of Fresenius, Classen, Treadwell, and Jannasch have also been consulted, and the book is indebted to them in many ways. It is also a pleasure to express my obligations to several friends for valuable advice and assistance, and especially to Prof. S. L. Penfield and Prof. L. V. Pirsson, to whom my first knowledge of, and training in, quan-

titative analysis are due. A number of most useful hints in manipulation were learned from these two analysts, all of which could not be specifically mentioned in their proper places, but which are acknowledged here. Acknowledgments are also due to the Trustees of the Carnegie Institution for permission to publish an analysis made under their auspices. The factors used in calculations are those given by Cohn in his recent translation of Fresenius' Quantitative Analysis.

All temperatures are given in centigrade degrees. The metric system is used generally, except in dealing with such pieces of apparatus as are usually sold in this country on the basis of English measurements.

HENRY S. WASHINGTON.

LOCUST, N. J., May, 1904.

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THE CHEMICAL ANALYSIS OF ROCKS.

PART I.

INTRODUCTION.

1. Importance of Chemical Analyses.

For the greater part of a century, since their study began, igneous rocks were regarded almost solely as more or less fortuitous mineral aggregates, these being usually assumed to be due to the fusion of previously existent rock bodies or to the mixture of several igneous magmas. With the introduction of the microscope, a more intimate study of their field relations, and especially with the improved chemical methods and the greatly increased number of satisfactory chemical analyses of the last twenty years, a decided change has come about in the way of regarding them.

Various observations and theories of the order of succession and of crystallization of minerals, differentiation of bodies of magma, consanguinity and petrographic provinces, have been made and advanced, all tending to throw light on the origin, genetic relationships and mode of formation of igneous rocks. Briefly put, the tendency of the modern study of igneous rocks is toward considering them as falling under Spencer's law of evolution; that is, in the general line of passage from an indefinite, incoherent homogeneity to a definite, coherent heterogeneity. In other words, the petrologist of the present day does not regard them as merely inert, solidified mineral aggre-

gates, whose characters are largely the result of chance conditions, but as bodies which bear in themselves evidences of the action of physico-chemical processes, and whose characters are determined by evolutionary laws. It is the aim of petrology to interpret these pieces of evidence and to ascertain the laws which govern their origin and formation. It is needless to say that this modern point of view renders igneous rocks objects of far greater scientific interest than they could have been under the older one.

For the proper study and understanding of these theoretical aspects of igneous rocks, the knowledge and application of some of the principles of physical chemistry are necessary, and it is obvious that for this a detailed knowledge of their chemical composition, as well as of their field relations, is essential. Conversely, it seems probable that the study of igneous rocks will be of service to the sister science of physical chemistry, since the petrologist is dealing in fact with solidified masses of solutions which have been formed and acted on by physico-chemical forces, under conditions of temperature, pressure and mass which it would be impossible to reproduce perfectly in the laboratory.

To the petrographer, who deals especially with the descriptive and systematic portions of the science, the chemical analysis of igneous rocks is assuming each year an increasing importance for their classification. Whether this is based only on the inherent characters of the rock-mass itself, or whether it takes account of genetic relationships, the chemical composition is becoming more and more an essential factor, and one which can no longer be relegated to the background, behind the superficially more prominent features of mode of occurrence, texture and qualitative mineral composition.

While our knowledge of metamorphic rocks is, as yet, not so far advanced as that of the igneous ones, their chemical composition plays, likewise, a most important part in their study and classification, and, to a certain extent, the same is true of the sedimentary rocks.

As regards the economic side of geology, the origin and formation of ores and useful mineral deposits, there is accumulating evidence of the importance of a knowledge of the chemical composition of igneous and metamorphic rocks. This refers, not only to their main features, but also to the occurrence in them of the less abundant elements, which by certain processes of segregation may become commercially available to us.

It is therefore evident that we possess in chemical analysis a means of investigation complementing, and of value fully commensurate with, the study of rocks in the field or with the microscope. That this is generally recognized is shown by the increasing prominence given to chemical analyses in recent petrological and petrographical papers, as well as in publications of an economic character. It is also shown by the increased attention given to this study by official organizations, and by the growing number of those who make, or who desire to make, their own analyses of rocks.

2. General Character of Analyses.

For a fuller understanding of the general subject, it will be as well to discuss briefly the factors which make up the character of a rock analysis, and which determine its value.*

The fulfilment of two conditions is essential to the value of a rock analysis: the specimen analyzed must be representative of the rock-mass, and the analysis itself must truly represent the composition of the specimen selected. The more closely both of these conditions are met, the greater will be the value of the analysis.

The representative character of the specimen is determined by the character of the rock-mass, as influencing both its selection and the amount of material taken for analysis. These points will be discussed subsequently (p. 43).

* This and the following section are a somewhat summarized statement of part of the discussion published in Prof. Paper U. S. Geological Survey, No. 14, pp. 16–43, 1903.

Assuming that the sample is representative of the rock-mass, the degree of correspondence between the figures yielded by the analysis and the real chemical composition of the rock is dependent on the two factors of accuracy and completeness.

By accuracy is meant the degree of precision with which the constituents sought for are determined, quite apart from whether or not all of those present have been determined or separated from one another. The accuracy of an analysis is dependent upon the methods used and upon the ability of the analyst to execute the various processes successfully. The purity of the reagents and the adequacy of the apparatus are also factors.

It must be borne in mind that no method is capable of yielding results of absolute accuracy, any more than it is possible to construct a mathematically exact geometrical figure. Certain sources of error are inherent in all, some of a general nature, and others of a character dependent upon the method in question. The analyst must rest content with reducing these to a minimum, by selecting methods which have been shown to be reliable. In this we cannot do better than follow the chemists of the U. S. Geological Survey, whose experience is of the widest, and who have set up a standard of analytical methods and practice for rocks and minerals that is beyond all others.

But the selection of proper methods is not the only desideratum. They must be carried out in a proper way, which will not lead to errors of a purely mechanical kind, and which may easily vitiate the results of the theoretically most accurate method. In this matter the analyst himself is the most important factor. He should have, not only sufficient knowledge of the facts of chemistry and of the principles of analysis to work understandingly, but also the dexterity and manipulative skill to enable him to carry out the various processes successfully. While it may be true of some analysts that, like poets, they are born, not made, yet granted intelligence and chemical knowledge and a fair amount of dexterity and application,

the necessary manipulative skill will come with practice, often in a surprisingly short time.

The analyst should beware of falling into careless habits or of allowing the analysis to become merely routine work. Carelessness is as fatal to obtaining good results as poor methods or impure reagents. During the whole progress of an analysis attention should be paid to every point of theory or manipulation, the influence of the various conditions or constituents should be considered, and indeed the analysis should be carried out from beginning to end with intelligent interest. This will turn into a pleasure what would otherwise be a dull and monotonous succession of precipitations, filtrations, ignitions and weighings, which, as has been justly said, is not chemical analysis.

That conscientiousness, a strict regard for the truth, and a firm determination to accept no result of doubtful character, are essential to the analyst, goes without saying.

As regards completeness, the ideal analysis should show the percentage amount of every constituent present, as well as the absence of those which might be expected but which do not exist in the rock. This is not always attainable, and for practical purposes the analysis should give figures for all constituents which are present in sufficient amount to make their determination a matter of interest, or whose presence or absence may bear on the problem for which the analysis is made.

The number of constituents which should be sought for and determined depends, of course, very largely on the character of the rock. Thus, in most granites, quartz-porphyries and rhyolites, which are of simple composition, comparatively few constituents need be determined to make the analysis satisfactory. On the other hand, in such rocks as nephelite-syenites, diorites, basalts, tephrites, etc., the number of constituents which should be determined is larger, and may easily reach twenty or more.

It is to be borne in mind that neglect to seek for some of the rarer constituents may lead to the overlooking of important

features, and that an analysis complete as to the subsidiary constituents may be of great value in the future, even if this degree of completeness is not necesssary for the end immediately in view. The aim of the analyst should be to turn out, as the petrologist should be willing to accept, only results of the highest character, so that it follows, as a general thing, that every analysis should be as complete as it is possible to make it.

The details of the constituents to be determined will be taken up later, but it may be stated here in a general way that all the main constituents must be determined in every analysis, as well as those minor ones which enter into the composition of minerals that are present in notable amount. If the general character of the petrographical province or the microscopical examination indicates the probable presence of certain of the rarer elements, these should also be looked for.

3. Microscopical Examination.

The chemical analysis should always be preceded by a microscopical examination of the rock in thin section. There are several reasons for this. In the first place, by a comparison of several specimens in thin section one is able to judge, better than by a merely megascopic examination, whether the specimen selected may be considered as really a representative one. It has happened in more than one instance that specimens selected for analysis without such microscopic study have been shown later to be abnormal forms and not typical of the rock-mass under investigation.

The microscope also frequently gives important indications to the analyst as to the presence of rare constituents which should be determined, or the absence of others which may therefore be neglected. He will thus often avoid neglecting constituents the determination of which may be of considerable importance, or, on the other hand, may save himself much labor and time in searching for substances which are not present, at least in determinable amount, which might otherwise be better spent.

Thus, if microscopic zircons are present in a granite, the amount of zirconia should be determined to render the analysis satisfactorily complete, while if these are absent this substance can be neglected without serious diminution in the value of the analysis. The presence of anhedra of a colorless, isotropic mineral, of low refractive index, will necessitate the determination of Cl and SO_3, as they may be of colorless sodalite or haüyne, while if none are found under the microscope in a holocrystalline rock these constituents may usually be considered as absent.

Finally, the thin section will show much more definitely than the hand specimen whether the rock is fresh and unaltered enough to justify its analysis.

It should also be noted that the percentage amount of certain constituents may sometimes be determined by the microscope with almost as much accuracy as by chemical analysis, and often with greater ease and expedition. This will be true for those which are present only in very small amounts and which occur in minerals of definite composition.

Thus, if zirconia is present only in zircon, or fluorine in fluorite, or sulphur in pyrite, the amount of these minerals in the rock can be readily estimated by Rosiwal's method,* and the percentage of ZrO_2, F or S respectively may be easily calculated. Though this method also applies to phosphoric anhydride in apatite, yet this substance is of such importance as a minor constituent, and its determination chemically is so easy and expeditious, that its amount should always be ascertained in the regular analytical way. In any case, except possibly for fluorine existing only in fluorite, this microscopical method is less satisfactory than the chemical, and if it is adopted, a note to that effect should be made in the statement of the analysis.

* Rosiwal, Verh. Wien. Geol. Reichs-Anst., XXXII, p. 143, 1898. Cf. Cross, Iddings, Pirsson, and Washington, Quant. Class. Igneous Rocks, Chicago, 1903, p. 204.

4. Constituents to be Determined.

Importance of Completeness.—In the earlier days of petrography the petrographer was quite content if the analyst reported figures for only eight or nine constituents, and he did not insist on the separation of the two oxides of iron. One seldom meets with analyses of this period in which TiO_2 or P_2O_5 are mentioned, to say nothing of such substances as ZrO_2, BaO or F. In the absence of exact knowledge of the mineral composition of rocks the presence of such rare elements was not suspected. Nor did neglect of them in the course of the analysis cause such low summations as to give rise to suspicions that something had been overlooked. This was partly because these rarer elements almost invariably occur in very small amounts, partly because some of them, as TiO_2, P_2O_5, ZrO_2, Cr_2O_3 and SrO, are precipitated and weighed with other constituents, and partly because the analyst of those days was not as accurate in his methods as at present, and was content with a summation which would cause the rejection of the analysis by a modern chemist.

After it became possible to study rocks in thin section, and when the use of heavy solutions made the separation of the component minerals easy, it was found that the number of chemical constituents commonly present in rocks was far larger than had been supposed, although the importance of determining them was not recognized for many years. With the improvement of old methods and the adoption of new ones, the determination of these minor constituents was greatly facilitated, and at the present day analyses in which figures are reported for twenty or more constituents are frequent; though, unfortunately, there is still a tendency among many chemists to rest content with the estimation of only the more notable ingredients.

At first sight it may not seem worth while to pay attention to constituents which are present only in amounts up to a few tenths of a per cent. But there are very good reasons for not neglecting them.

For one thing, the determination or not of some of them may affect, and in some cases seriously, the figures for other and more important constituents. This is due to the fact that several of them are precipitated and weighed together, and then all except one separately determined, the figures for the final one thus depending on those of the others. Thus, Al_2O_3, Fe_2O_3, TiO_2, MnO, ZrO_2 and P_2O_5 are thrown down and weighed together, all except alumina separately determined, and the Al_2O_3 ascertained from the difference. It is evident that if any of these other oxides are neglected the figure for alumina will be too high, and in some cases this will give rise to serious error. A similar case is that of CaO and SrO, though here the error involved will seldom be of great moment.

Another, and equally important, reason is that evidence is accumulating, as analyses of a high degree of completeness become more common, that much light may be thrown upon problems of great interest by a knowledge of the presence of the rarer elements. The subject has been discussed by Hillebrand,* whose strong plea for completeness it will be well for the student to read. An illustration given by Hillebrand may be cited here. The analyses of the U. S. Geological Survey show that BaO and SrO are almost invariably present in the igneous rocks of the United States, and that the former is uniformly in greater quantity than the latter. Furthermore it is made clear that, while never present in large amount, they are both more abundant in the rocks of the Rocky Mountain region than in those to the east and west of this. As Hillebrand says: "Surely this concentration of certain chemical elements in certain geographical zones has a significance which future geologists will be able to interpret, if those of to-day are not."

Another interesting result of the determination of the rarer elements is the discovery that certain of them are associated more especially with magmas of certain characters, but are seldom found in rocks derived from magmas of other chemical

* W. F. Hillebrand, Jour. Am. Chem. Soc., XVI, p. 90, 1894; Chemical News, LXIX, p. 209, 1894; Bull. U. S. Geol. Surv., No. 305, p. 18, 1907.

types. Thus it has been shown that vanadium is apt to occur among the more basic rocks, while it is absent, or nearly so, in those which are high in silica; and conversely, that molybdenum is apparently confined to the more siliceous rocks but is absent from the basic ones. It is now well known that zirconium is especially abundant in rocks which are high in soda, and also that it is a frequent ingredient of granites and other rocks very high in silica. On the other hand, chromium and nickel are seldom met with in rocks not high in magnesia and low in silica. Gold, silver and platinum are occasionally found as apparently primary constituents of igneous rocks, but the first two are found either in acid rocks or in diabase, while the latter seems to be confined to the peridotites.

This leads directly to the consideration of a final point in favor of the present contention. This is the light that may be thrown on the origin and formation of ores, and the possibility of such chemical study of the igneous and metamorphic rocks leading in the future to important economic advances in the indication of the presence of ore bodies. The researches of Sandberger and others * have shown that many of the heavy metals, such as antimony, arsenic, bismuth, cobalt, copper, lead, silver, tin, uranium, and zinc, are present in the pyroxenes, hornblendes, biotites and olivines of some igneous rocks, and can be readily detected if sufficiently large amounts are taken for investigation. Further consideration of this topic is uncalled for here, but, from the point of view of the mining engineer and of geological surveys, it is clear that this is a weighty argument in favor of completeness in the making of chemical analyses of rocks.

While it follows from the above that all rock analyses should be as complete as it is possible to make them, yet the practical considerations of time and labor may set limitations on this. Although by judicious management a number of the minor con-

* F. Sandberger, Zeits. Deutsch. Geol. Ges., XXXII, p. 350, 1880; Zeits. Prakt. Geol., 1896; cf. J. H. L. Vogt, Zeits. Prakt. Geol., 1898, pp. 225 ff.

stituents can be determined along with the main ones, and at the cost of very little extra time, it is true that a thoroughly complete analysis will take considerably longer than a simple one. The analyst must judge for himself how far he can profitably go in this way, but it should always be borne in mind that a few complete analyses will probably be of more value in the end than a larger number of incomplete ones.

While it is probable that all or nearly all of the known elements may occasionally be present in rocks, and can be detected if sufficiently large amounts are taken for analysis, in practice we must, for the purposes of this volume, confine our attention to those which may reasonably be looked for in igneous, metamorphic and many sedimentary rocks, and which may be readily estimated in quantities of from one-half to two grams of material. Those which will be considered in this book are given in the following list, which is substantially that of Hillebrand:*

SiO_2, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, FeO, MnO, NiO, CoO, CuO, MgO, CaO, SrO, BaO, K_2O, Na_2O, Li_2O, H_2O, CO_2, P_2O_5, Cl, F, SO_3, S.

In addition, in certain cases such rare elements as thorium, cerium, didymium, yttrium, zinc, glucinum, boron, tin, nitrogen or carbon (as graphite or organic matter) may be present in notable amounts, as shown by the occurrence of certain minerals containing them, but these instances are so rare, and their determination involves such complicated methods, that they will not be considered here.

In the great majority of rocks the constituents of the list just given are by no means of equal importance, and it is customary to divide them into "main" and "minor" constituents.

Main Constituents.—Speaking generally, the main constituents are SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O.

These nine (including both oxides of iron) are almost invariably present in greater or less amount in all igneous and metamorphic silicate rocks, and must certainly be determined

* Hillebrand, Bull. 176, p. 20; Bull. 305, p. 21.

if the analysis is to conform to even the first requirement as to completeness.

The only possible exceptions would be certain rare and little-known types, with which the average student is not likely to meet. Thus, in iron ores produced by differentiation of an igneous magma, or in dunites, the amount of alkalies may be so small as to be negligible for most purposes. Or, in the case of very highly quartzose dikes of igneous origin, such as have been described by Howitt in Australia, the determination of CaO and especially MgO may be omitted. But even in such cases it is far better to prove definitely that such constituents are absent or present, even if only in traces. In the light of physico-chemical investigations of extremely dilute solutions, such knowledge may be of great interest and importance in the future.

Stress must be laid on the importance of the separate determination of both oxides of iron, which are only too often unseparated and reported in the analysis as either Fe_2O_3 or FeO. Neglect of this point was especially common up to twenty years ago, and is the cause of the relative worthlessness of many of the older analyses.* It is clear that, as the two oxides play different rôles in the composition of minerals, a knowledge of the relative amounts of each is absolutely necessary to a thorough understanding of the rock magma, the calculation of the mode (actual mineral composition) of the rock, or for its classification along chemico-mineralogical lines. Although the error involved by their non-separation may be small in certain highly quartzose or feldspathic rocks, in which they do not amount collectively to more than one or two per cent, yet the conscientious analyst should make it a point to determine them separately in every case.

While the amount of water is not vital to our knowledge of the rock magma, except in the case of the presence of minerals containing water of crystallization or hydroxyl, as analcite and muscovite, yet it is important as giving a measure of the fresh-

* Cf. H. S. Washington, Prof. Paper U. S. Geol. Surv., No. 14, pp. 24 and 43, 1903; Prof. Paper U. S. Geol. Surv., No. 28, p. 15, 1904.

ness of the rock. It is also usually present in very notable amount, and should therefore be reported in every rock analysis. There is all the more reason for this on account of the ease and celerity of the determination, and the fact that its neglect will seriously affect the summation of the analysis in nearly all cases. It is also evident that the determination is essential in the investigation of many metamorphic and sedimentary rocks, and in the study of rock weathering and alteration, where hydrous minerals, as chlorite, zeolites and limonite, are present.

As will be seen later, it may exist as either "hygroscopic" or "combined" water, which are expelled from the rock powder at temperatures respectively below and above about 110°. There is considerable difference of opinion as to the advisability of the separate determination of these, as well as to the reporting of the hygroscopic water in the analysis. The arguments for and against their separation have been discussed by Hillebrand,* and need not be repeated here. It may suffice to say that the author coincides with the opinion of Hillebrand in recommending their separate determination and inclusion in the statement of the analysis, and the use of air-dried material for analysis.

Apart from the constituents discussed above, there are a number of others (usually minor ones), which may at times assume equal importance with, or even far surpass, some of them. While such cases are uncommon, yet their number is rapidly growing with increase in our knowledge of the less well-known rocks of the globe, and most of them are of special interest from the theoretical side. As examples there may be cited titaniferous ores produced by differentiation, as those of the Adirondacks, the apatite-syenites of Finland, such sodalite- and haüyne-rich rocks as tawite, taimyrite, and the Italian haüynophyres, the eudialyte-rich lujavrites of Kola and Greenland, or the apparently igneous pyritiferous ores of Norway. In these, certain constituents which are usually regarded as minor, TiO_2, P_2O_5, Cl, SO_3, ZrO_2 and S, respectively, are of an importance almost or

* Hillebrand, Bull. 176, p. 32; Bull. 305, p. 54.

fully equal to that of any of the nine mentioned above, and it is self-evident that an analysis of such rocks which does not take them into account is fatally defective.

Minor Constituents.—Turning to the minor constituents, it will be found that they differ much in importance. Some of them are precipitated and weighed with certain main constituents (as has been mentioned above), and their weight afterward subtracted from that of the mixed precipitate. Therefore, if they are neglected, the apparent amount of the main constituent, which is determined by difference, will be too large. This is the case, for instance, with TiO_2, ZrO_2, Cr_2O_3, V_2O_3 and P_2O_5, which, if disregarded, will increase the quantity of alumina by their weights. The resultant error may not be very large, but, being an avoidable one, should not be committed by the careful analyst.

This is especially true of TiO_2 and P_2O_5, which are almost invariably present and often in quantities sufficiently large, if neglected, to cause serious error in the figures for Al_2O_3. These two should therefore be determined in every analysis, or its value may be seriously diminished, as the knowledge of the exact amount of alumina is a very important factor in certain chemico-mineralogical rock classifications, as well as in the calculation of the mineral composition. In regard to the other three, ZrO_2, Cr_2O_3 and V_2O_3, they are seldom present in amount greater than a few tenths of a per cent and usually less, so that neglect of them will seldom involve appreciable error in the figures for alumina. Zirconia is usually the most important of them, especially in rocks of a certain character, and it is always well to determine this, as may be done for the other two, if there seems to be sufficient warrant for it.

Falling under the same category are SrO, Li_2O and MnO. The first of these is precipitated along with CaO and weighed with it, being afterward separated from it to arrive at the true amount of lime. Similarly Li_2O is weighed with Na_2O, thus increasing its apparent amount. But both strontia and lithia are present in such minute quantities, especially the latter, that

their non-determination will not affect the figures for lime and soda to any great extent. They are chiefly of interest from the theoretical side, and this applies more especially to strontia.

The case of MnO is somewhat complex and debatable, and for its discussion we must anticipate the description of some features of its method of determination. Under some circumstances it is precipitated in part by ammonia water, so that, if only this reagent is used for the precipitation of alumina, iron oxides, etc., some of it may be thrown down and weighed with them, and will ultimately affect the weight of alumina. Part of that in the filtrate is precipitated with the CaO as oxalate, if the manganese has not been separated by ammonium sulphide, and the rest will fall with the MgO as phosphate. It is clear, therefore, that unless the manganous oxide is completely separated from the alumina, etc., and if it is not precipitated before determination of lime and magnesia, it will be distributed among these three constituents. An investigation of this distribution by G. Steiger* indicates that it is real but quite variable. If once partially precipitated with the alumina the manganese tends to remain with this on solution and reprecipitation. The amount thrown down with magnesia as phosphate is apt to be greatest, while that precipitated with lime as oxalate is least.

On the other hand, manganese is completely separated from alumina and iron by the basic acetate method, but in this the precipitation of Al_2O_3 and Fe_2O_3 is apt to be not quite complete, unless the conditions are very exactly controlled, which is somewhat difficult for the inexperienced analyst. Unless separated, the small amounts of Al_2O_3 and Fe_2O_3 left in solution will then be precipitated later with the MnO and weighed with it, thus giving rise to abnormally high figures for MnO and correspondingly low ones for the two sesquioxides. This error seems to be a fairly frequent one.

In considering this matter account must be taken of the

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* Hillebrand, Bull. 305, p. 96.

fact that the total amount of MnO is almost invariably very small, only exceptionally over 0.50 per cent, and usually much under 0.20 per cent, these estimates being based on the most reliable analyses.* Bearing this in mind, as well as the fact that the basic acetate method in the hands of the inexpert is very liable to cause serious error in the figures for Al_2O_3 and to a less extent for Fe_2O_3, I strongly recommend the avoidance or abandonment of the basic acetate method and the precipitation of the alumina, etc., by ammonia water. The precipitation may be made either with or without the presence of ammonium persulphate; in the former case the manganese falling wholly with the alumina, and in the latter being distributed in unknown proportions between the alumina, lime, and magnesia, though the error involved for each will be very small as a rule. On the whole my personal preference is in favor of precipitation in presence of persulphate, unless the rock is very rich in lime. The manganese is to be determined in a separate portion by the easy and rapid colorimetric method, so that manganese is one of the minor constituents which should be always determined in any rock analysis making pretense to accuracy or completeness.

Another point in this connection, though of subsidiary importance, is that the gravimetric determination of MnO lengthens the time needed for completing the analysis by at least a day, and in view of the comparative unimportance of this constituent, it would seem to be preferable to save this time and to devote it to other analytical work of greater interest.

The second category of minor constituents consists of those whose determination or not does not effect the figures for any of the main ones. This would include NiO, CoO, CuO, BaO, S, SO_3, Cl, F and CO_2.

Of these, the first three occur in igneous rocks as a rule only in minute traces, and the first two are apt to be found in the most basic ones, especially peridotites. In such rocks

* J. H. L. Vogt, Zeits. Prakt. Geol., 1898, p. 235; H. S. Washington Prof. Paper U. S. Geol. Surv., No. 14, p. 27, 1903.

they may well be determined. Indeed, the determination of nickel is advisable in all very particular analyses of intermediate to basic rocks, especially if economic problems are involved, though neglect of it will seldom if ever lead to serious error in dealing with terrestrial rocks. Copper cannot be considered an important constituent, but it can well be looked for in basic rocks, as it may be of theoretical interest.

As has been mentioned above, barium is a constant constituent of the igneous rocks of the United States, and it is almost certain that it will be found to be widely distributed elsewhere when it is systematically looked for. In view of its theoretical interest and the comparative ease of its determination by the method given beyond, it will usually be advisable to look for it in the course of the analysis.

Sulphur is very frequently present as the sulphides pyrite and pyrrhotite, and indeed much more often than was formerly believed, especially in the more basic rocks. Its amount can be readily ascertained along with the BaO and should enter into the statement of most analyses, or its absence definitely shown.

Sulphuric anhydride and chlorine are met with in igneous rocks with comparative frequency, and both are always to be estimated if minerals of the sodalite group are present. It is always well to determine them in rocks liable to carry such minerals, even if not visible with the microscope. In other cases also it can scarcely be held to be a great loss of time to look for them, in view of their possible theoretical interest and the ease of their determination.

Fluorine is seldom present in quantities over a few tenths of a per cent, and, as its determination is somewhat lengthy and laborious, it need not often be looked for. However, this may be done if the rock contains fluorine-bearing minerals, but even here its determination is necessary only if these are abundant or for very accurate work.

Carbon dioxide is often present in igneous and metamorphic silicate rocks but, as far as is now known with certainty, only

when the rock is not strictly fresh, as a component of the secondary minerals, calcite, dolomite, siderite and cancrinite. If it is present it should always be determined, as it serves to a certain extent as a measure of the freshness of the rock, and as the result may have a bearing on the problem of its occurrence as a primary constituent.

5. The Occurrence of Various Elements.

The increased number of analyses of igneous rocks, especially of unusual types, and the more frequent determination of the minor constituents, with the vast mass of data obtained by the use of the microscope, have shown that certain of the rarer elements are prone to occur in rocks of certain chemical characters. While our knowledge along this line is far from complete, a few words may be devoted to this subject, as it will often be of use to the analyst to know which elements should be especially looked for and which may safely be neglected.* The various minerals which carry the several elements in question will also be mentioned as well as the amounts in which the elements usually occur.

Titanium is invariably present, as shown by all rock analyses in which it has been sought for, and it is ninth in order of abundance among the elements making up the crust of the earth. It exists in very small amount in the more quartzose and feldspathic rocks and most abundantly in the more basic. It is an essential component of ilmenite and perofskite, which are most common in basic rocks, and of titanite, which occurs in rocks with more silica. The oxide rutile is rare in igneous rocks, but is more common in metamorphic ones. Titanium also enters into some magnetite and hematite, and also very commonly, but to a less extent, into pyroxenes, amphiboles,

* See also F. W. Clarke, Bull. U. S. Geol. Surv., No. 78, pp. 34–42, 1891; J. H. L. Vogt, Zeits. Prakt. Geol., 1898, pp. 225 ff.; F. W. Clarke, Bull. U. S. Geol. Surv., No. 168, pp. 13–16, 1900; J. F. Kemp, Ore Deposits of the United States, New York, 1900, p. 35; Hillebrand, Bull. 305, p. 21; H. S. Washington, Trans. Am. Inst. Min. Eng., XXX, p. 809, 1908; J. P. Iddings, Igneous Rocks, I, 1909, p. 27.

biotites, garnets and other ferromagnesian minerals. Its amount in rocks may vary from traces, seldom being over one per cent, to five or more per cent.

Zirconium is present in many rocks in small amount, but is most apt to occur in granites, pegmatites, rhyolites, syenites, and in nephelite syenites, phonolites, tinguaites and tephrites, and is most abundant in rocks which are high in soda, such as the last four. It is rarely met with in the more basic rocks, especially those rich in lime, magnesia and iron. Zirconium is usually found as the silicate zircon, especially in granites and syenites, but is also an ingredient of such rare minerals as eudialyte, låvenite and rosenbuschite. Zirconium is present usually in amounts up to .20 per cent of ZrO_2, but may reach 2 per cent or more.

Chromium is almost wholly confined to the basic rocks, especially those which are high in magnesia and low in silica, and consequently contain abundant olivine, such as peridotite and dunite. It occurs as chromite and picotite (chrome-spinel), and in some augites, biotites and olivines. It may occur up to one-half of one per cent of Cr_2O_3.

Vanadium, according to the investigations of Hillebrand, "predominates in the less siliceous igneous rocks and is absent, or nearly so, in those high in silica." It is an ingredient of pyroxenes, hornblendes and biotites, but not of olivine, and is also found as an ingredient of ilmenite in titaniferous iron ores. Its amount is always very small, seldom over 0.05 per cent.

Manganese is uniformly present in nearly all rocks, but its amount is small, generally in tenths of a per cent, only very exceptionally one-half of one per cent or more. The high figures commonly reported are, in most cases, due to analytical error, an opinion in which Dr. Hillebrand concurs. It occurs in the ferromagnesian minerals, pyroxenes, amphiboles, micas, olivines, etc., and therefore is usually present in greatest amount in the more basic rocks. It seems to favor rocks high in iron rather than those high in magnesia.

Nickel and cobalt, like chromium, are most abundant in

olivine rocks, but the former has been noted in certain basalts. They occur as ingredients of olivine, as well as in pyrite and pyrrhotite, and in hornblende and biotite to a small extent. The amount of nickel in terrestrial rocks is seldom more than 0.05 or 0.10 per cent, while that of cobalt is only exceptionally more than a trace. In some cases nickel has been undoubtedly reported too high, as has been the case with manganese, probably having been confounded with contaminating platinum.

Copper is often to be found in igneous rocks, but as a rule merely in traces. It is probable that the copper reported in some analyses of igneous rocks is really platinum derived from the platinum basin and crucibles, while again it may be due to contamination from the water baths, etc. It is most frequent in the more basic rocks, such as diabase, gabbro and basalt, entering the pyroxene and amphibole, as well as being a component of chalcopyrite, and in traces in some pyrite. It also occurs as the metal.

Barium and strontium are very commonly present in igneous rocks, the latter uniformly in less amount than the former. There is considerable evidence that barium is apt to be most abundant in rocks which are high in potash. Barium occurs in the feldspars, especially orthoclase, as the celsian molecule, in the rare hyalophanes, in some zeolites, as well as in a few biotites and muscovites. We can, at present, form no definite conclusion as to the character of the magmas most likely to carry strontium, and analytical data on this point would be of interest. The amount of BaO may reach one per cent, though usually much less, while that of SrO may run up to 0.30 per cent, but, as a rule, is little more than a trace.

Lithium is an element of very wide-spread occurrence, but is seldom met with in rocks in more than spectroscopic traces. It may naturally be expected to be most abundant in highly alkalic rocks, and there is reason for the belief that it is especially prone to occur in sodic ones. Apart from its occurrence as an essential constituent of such minerals as lepidolite and spodumene, which occur in highly acid pegmatites and granites,

it is also found in the alkali feldspars, muscovite, beryl and other minerals.

Phosphorus is almost invariably present in igneous and metamorphic rocks, like titanium, and like this element it is most abundant in the more basic ones, especially in those which are high in lime and iron rather than in magnesia. It occurs almost solely in apatite, or very exceptionally as xenotime or monazite. While the quantity of P_2O_5 usually runs from 0.10 to 1.50 per cent, generally under one, it may occasionally amount to much more.

Sulphur, as sulphides, is far more abundant in the basic rocks of all kinds than in the acid ones, and forms an essential ingredient of pyrite and pyrrhotite, and the rare mineral lazurite. As sulphuric anhydride (SO_3) it occurs only in the minerals haüynite, noselite, and lazurite, and usually in the more basic rocks, though some haüynite rocks carrying quartz are known. These last three minerals are most apt to occur in rocks which are high in soda. Sulphur, as sulphides, is present usually in tenths of a per cent, as is also true of SO_3, though in certain cases the amount may be much higher. It is a common error to report sulphur as SO_3 instead of as S (Hillebrand).

Chlorine is present most abundantly in rocks which are high in soda, and especially when so low in silica that nephelite is present, though it is also found sometimes in nephelite-free rocks, and in a few cases in quartz-bearing ones. It is an essential component of sodalite and noselite, and is also present in scapolite and in a few apatites. It also occurs, as sodium chloride, in fluid inclusions. The amount of Cl is usually in a few tenths of a per cent, but in rare cases it may be one per cent or more.

Fluorine as a component of apatite, biotite, etc., seems to have no special preference as to magma, though, on the whole, it is found more frequently in acid than in basic rocks. It is, however, most apt to be met with as fluorite and some other rare fluorine minerals, in rocks containing nephelite, as foyaites and tinguaites. It is an essential constituent of fluorite and most apatite, and as an integral part of the last mineral is

almost universally present. It also occurs in biotites and other micas, in some hornblende and augite, as well as in tourmaline, topaz, chondrodite, etc. Its usual amount is very small, generally from traces to 0.10 per cent, only rarely getting above the latter figure.

Of the other rare elements it may be of interest to the student to note the following. Glucinum, as a component of beryl and some other very rare minerals, is most frequent in granites, pegmatites and quartzose gneisses. It seems to be most at home in sodic rocks. There is reason to think that the high alumina sometimes reported for these rocks may be in part glucina, which has not been separated from the alumina, and due to the presence of unidentified beryl. This is a point worthy of investigation. Tin, as cassiterite, is confined to the acid rocks, granite, quartz-porphyry and rhyolite, and its presence is due generally to pneumatolytic processes. Apart from cassiterite, it occurs in traces in ilmenite, micas and feldspars. The rare earth metals occur in allanite, which is of widespread occurrence in small amounts in many granites, xenotime, monazite, and other minerals of even greater rarity, and seem to be especially frequent in acid rocks and possibly those with much soda. Molybdenum, tungsten and uranium are almost exclusively confined to the very siliceous rocks. Zinc has been met with in granite, as well as in basic rocks, but no generalization in regard to it is possible as yet. Platinum is found almost exclusively in peridotites, but is occasionally met with in connection with gabbros. Boron, as a constituent of tourmaline, is most apt to occur in highly siliceous rocks.

6. Summation and Allowable Error.

In the ideally perfect analysis, of course, the summation will be exactly 100, but in practice, as is well known, this result is seldom attained, and if so must usually be regarded as due to the compensation of different slight errors of excess and deficiency. As has been already remarked, no analytical methods are wholly

free from sources of error, and the aim of the analyst must be to reduce these to as small dimensions as possible.

As Hillebrand has stated,* "A complete silicate rock analysis which foots up less than 100 per cent is generally less satisfactory than one which shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however carefully purified, still contain, or extract from the vessels used, traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering an analysis from first to last is very considerable, washings of precipitates may be incomplete, and if large filters are used for small precipitates the former may easily be insufficiently washed."

On the other hand, deficiencies in the summation may be due to mechanical loss of substance through spilling of drops, etc., too much washing, which may result in the partial loss of slightly soluble precipitates, and finally to the non-determination of some of the constituents which are actually present.

The limits of summation below or above 100 per cent which may be considered as allowable and consistent with satisfactory analysis are stated by Hillebrand as 99.75 and 100.50, but for the usual run of analytical work they may fairly be extended to 99.50 and 100.75. If the analyst attains summations within these limits he may consider his results as satisfactory, provided that there is no reason to suspect the possibility of errors having been made which compensate each other. If the analysis foots up considerably under the lower limit, especially in several analyses of a series of similar rocks, the probability of some constituent having been overlooked becomes strong. If this is not the case, and also if the summation is much above 100.75, the analysis should be repeated in whole or in part, to discover the cause of error. As Hillebrand remarks, "It is not proper to assume that the excess (or deficiency) is distributed over all determined constituents. It is quite as likely, in fact more than likely, to affect a single determination and one which

* Hillebrand, Bull. 176, p. 24; Bull. 305, p. 25.

may be of importance in a critical study of the rock from the petrographic side."

There are several special cases of high or low summations which are due to the determination of various constituents, and which therefore do not indicate inferiority in the analysis as a whole. If water be determined by loss on ignition the total will usually be lower than it would be were the water determined directly. This is owing to the partial oxidation of the ferrous oxide in the rock, and a consequent apparent amount of water less than that which really is present.

If the iron oxides are not separately determined, but are given as ferric oxide, the sum will be too high by one-ninth of the amount of ferrous oxide present, and conversely, if they are given as ferrous oxide alone, the sum will be too low by one-tenth of the ferric oxide present. This cause is, of course, eliminated when both are determined.

If the analysis shows the presence of Cl, F or S, an amount of oxygen equivalent to these must be deducted, or the sum of the analysis will be too high by that amount. The oxygen equivalent of chlorine is 0.22 Cl, of fluorine 0.42 F, and of sulphur 0.43 S, if it exists only in pyrrhotite. As regards the sulphur of pyrite, while Hillebrand * has shown that it is attacked by sulphuric and hydrofluoric acids only to a scarcely appreciable extent in the course of the determination of ferrous oxide by the methods given later, yet the iron with which it is combined will be given in the statement of the analysis as ferric oxide. Consequently the oxygen equivalent of sulphur in pyrite is 0.375 S, instead of 0.25 S, as it would be were its iron content determined as ferrous oxide.

To give an example of the application of these corrections, if the sum of an analysis is 100.28 and there is 0.54 Cl present, we must deduct $0.54 \times 0.22 = 0.12$, leaving 100.16 as the correct summation.

In the earlier days of analysis chemists and petrographers

* Hillebrand, Bull. 176, p. 95; Bull. 305, p. 138.

alike were content with summations which fell below 99, or were above 101, and it is to be regretted that the same complacency has not become quite extinct at the present time. But the conscientious analyst should look upon such figures with the gravest suspicion, and reject all analyses which furnish such manifestly erroneous results, as they are very strong evidence that the analysis is faulty either in part or throughout.

In attempting to allot the allowable limit of error for each constituent, regard must be had to its amount in any given case. Assuming that the allowable total error is ± 0.60, which is not quite correct, but near enough for the present purpose, we might allot this proportionately among the chief constituents somewhat as follows. Taking, for example, the average igneous rock as calculated by Clarke * we would obtain these figures: SiO_2 ± 0.35, Al_2O_3 ± 0.10, Fe_2O_3 ± 0.02, FeO, MgO, CaO and Na_2O ± 0.03, K_2O ± 0.02, H_2O and TiO_2 ± 0.01. These are based on the assumptions that the errors would be all in one direction and proportional to the amount of each constituent. As, however, we cannot always expect such close agreement in duplicate determinations of the less abundant constituents, and as the various errors are almost certain to compensate for each other to some extent, we may provisionally assume the figures below as allowable limits of error in cases of constituents present in about the following amounts. The limits here given are percentages of the whole rock, not of the amount of each constituent. For SiO_2 and others which amount to 30 per cent or over, from 0.20 to 0.30; for Al_2O_3 and others which amount to from 10 to 30 per cent, 0.10 to 0.20; for constituents which amount to from 1 to 10 per cent, 0.05 to 0.10.†

* F. W. Clarke, Bull. U. S. Geol. Surv., No. 168, p. 14, 1900.

† An experimental examination of the amount of allowable error has been made by M. Dittrich (Neues Jahrbuch, 1903, II, p. 69), by the analysis of known mixtures of the different rock constituents. He comes to the conclusion that the errors for each are in general in one or the other direction, and establishes limits of magnitude similar to those given here. As, however, all the methods employed by him are not those recommended in this book, his figures are not appropriate for an analysis according to these la-t.

These figures are rough, and based on experience in analysis rather than on mathematical calculations. They merely indicate that duplicate determinations should not differ from each other by more than about these amounts, although the difference may sometimes be considerably greater than these without reflecting seriously on the character of the analysis. At the same time the student should not consider that the latitude thus granted by such allowable limits of error justifies him in taking advantage of them as an excuse for poor work. He should, on the contrary, endeavor to make his analyses so that the differences between duplicate determinations, if they are made, fall well within the limits thus allowed.

Indeed, it should be made an invariable rule by the novice to make duplicate analyses throughout, until he becomes familiar with the methods and manipulations, and by repeated close agreements may place justifiable confidence in single determinations. This will at first involve more labor and the turning out of fewer analyses in a given time, but the increased value of the results will more than compensate for this in the end. An analysis in which the analyst himself cannot place implicit confidence is not only of little use but positively dangerous for others, for whom there may be no evident reason for doubting the results, and such work will eventually reflect injuriously on its author.

In regard to duplicate* analyses, however, it must be remembered that close correspondence in two separate determinations is not, in itself, conclusive proof of correctness. Practically identical results may be obtained several times on repetition by poor as well as good methods, and if the same errors are made in duplicate analyses the figures in each may agree closely and yet be far from the truth. At the same time, the chances are decidedly against obtaining duplicate results so closely concordant as to be satisfactory, in the case of poor methods, and especially if errors of manipulation have been committed, so that duplicate figures which agree well with

* Cf. Penfield, Am. J. Sci., X, p. 21, 1900.

each other justify, on the whole, a high degree of confidence in their correctness.

7. Statement of Analyses.

The results of the analysis might be stated either in terms of the elements present or of the basic oxides and acid radicals. While the former may be the more logical on purely theoretical grounds, yet the latter greatly facilitates calculations based on the analytical data, and being universally in use, renders comparison of all rock analyses with each other very simple. It should therefore be adopted without question.

The order in which the constituents are tabulated varies somewhat widely. In some cases the order is roughly that in which the constituents are determined in the course of the analysis. Elsewhere one finds the acid radicals placed first, followed by the basic oxides. Or SiO_2 is followed immediately by Al_2O_3, or sometimes by TiO_2, and then the more important basic oxides, generally including MnO, with the less abundant constituents following these.

There is unanimity only in heading the list with SiO_2. In regard to all the other substances reported there is very considerable diversity in the details of succession. Thus CaO sometimes precedes and sometimes follows MgO, and the same is true of Na_2O and K_2O. This lack of uniformity is to be deplored, as it is not only extremely apt to lead to error in copying analyses the order of which is unfamiliar, but renders the comparison of two or more tabulated according to different systems needlessly difficult.

Some years ago it was proposed * that petrographers and chemists follow a definite and uniform plan in the statement of the analyses of rocks, and the order then suggested with the reasons for its adoption are briefly given here. It may only be added that no cogent reason has been brought forward for any important modification, and that it has been adopted in its essentials by the chemists of the U. S. Geological Survey.

* H. S. Washington, Am. J. Sci., X, p. 59, 1900.

The general foundation for the order proposed is that analyses of rocks are intended primarily for the benefit of petrographers and petrologists, so that an arrangement along analytical or strictly chemical lines is neither advantageous nor appropriate. To them the eight oxides, SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O and K_2O, which are present in the vast majority of rocks in preponderating amount, are, and must always remain, of prime importance. H_2O and CO_2, which are also often present to a very notable extent, are of value as measures of the freshness of the rock. The other constituents, while of varying interest, are usually present in small or minute quantities, and influence the character of the rock only to a limited extent. The order suggested, with a few slight modifications, is:

SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O+(ignition), $H_2O-(110°)$, CO_2, TiO_2, ZrO_2, P_2O_5, SO_3, Cl F, S (FeS_2), Cr_2O_3, V_2O_3, MnO, NiO, CoO, CuO, (ZnO), BaO, SrO, Li_2O.

By putting the eight main oxides together and at the head, the general character of the rock is seen at a glance. Furthermore, whether an analysis is complete or incomplete, these oxides are always in the same relative position, and, as they are determined in every case, the eye finds them without trouble, thus immensely facilitating comparison and study.

As regards the main portion, we start out with the chief acid radical and the constituent which is present in largest amount, and pass through successively lower orders of oxides to the most positive bases, the alkalies. At the same time they are presented in a way which brings the oxides together in their natural petrographic and mineralogic relations. Alumina, which often plays apparently an acidic rôle and which is usually the most abundant constituent next to silica, follows immediately after this, and is succeeded by the other main sesquioxide, ferric oxide. Ferrous oxide follows ferric, and magnesia is next to it, as the two go hand in hand in the ferromagnesian minerals. Lime comes next in an intermediate position between these and the alkalies, as is proper, because it is a con-

stituent both of the ferromagnesian minerals and of the feldspars. Soda precedes potash, as it is associated with lime in the plagioclases.

Water follows immediately after the main oxides, since it is a highly important and generally determined constituent. Combined water precedes hygroscopic, being the more important and usually present in greater amount than the latter. Carbon dioxide comes next, as it, with water, is a measure of the freshness of the rock, and this character can therefore be told at a glance. They also constitute together the "loss on ignition" so frequently given, and may then be connected by a bracket in comparative tabulations.

Of the minor constituents the acid radicals come first, following the main principle of the other division. Titanium and zirconium dioxides are placed at the head, as they are chemically similar to silica, and often replace it. Phosphoric anhydride comes next as being usually, next to TiO_2, the most important and most abundant of the minor constituents. Sulphuric anhydride and chlorine are together, since both are constituents of the sodalite group of minerals. Fluorine, also a halogen, follows after chlorine. Sulphur completes the list of minor acid radicals, being less acidic than most of these, and being also frequently present as an apparently secondary constituent, and hence analogous to water and carbon dioxide among the main ones.

The subordinate metallic oxides follow in the order R_2O_3, RO and R_2O. Chromium sesquioxide precedes vanadium as the more important. These two might be placed among the minor acid radicals, but the position chosen seems the best. Manganous oxide precedes the oxides of nickel and cobalt, as it is very frequently determined, and is usually present in greater amount. The monoxides of the other heavy metals when present come next, those just mentioned preceding on account of their greater importance and their chemical affinity with ferrous oxide. Of the oxides of the minor alkali-earth metals, which are next in order, baryta precedes strontia as

the more abundant and important. Lithia follows as the only representative of the alkali metals.

In stating the analysis it may be recommended that the molecular ratios of each of the constituents, obtained by dividing the percentage amount by the molecular weight, be given along with the regular statement. The user of the analysis will thus be saved the trouble of calculating them for himself, and the chemical character of the rock will be more fully and immediately comprehended. A list of the molecular weights of the various chemical constituents will be found on another page (p. 189).

In the statement of analyses the term "trace" is in frequent use, to indicate that a constituent is present, or supposed to be present, in a small but undetermined amount. The use of the term has been loose, and in some cases quite erroneous, as more complete analyses have shown that such "traces" may amount in reality to one-half, or possibly one or more, per cent. It would be better to have the meaning of the term more strictly defined, and it has been suggested * that it "should indicate strictly and uniformly that the constituent (to which it is applied) has been looked for and found, but in unweighable amount (0.1 milligram or less)." If there is no knowledge as to the presence of a substance a dash may be used. Hillebrand suggests that, "In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present." For this purpose the letters "n. d." (not determined) may be reserved.

The analytical calculations should be carried to four decimals, which implies that in the statement of analyses the figures are to be given to hundredths of a per cent. While the last decimal may not be of much significance, it represents the limit of weighing (0.0001 gram) in the quantities taken for the determination of the constituents of rocks, and gives some assurance of the value of the preceding decimal. It

* H. S. Washington, Prof. Paper U. S. Geol. Surv., No. 14, p. 24, 1903.

is also the almost universal practice among chemists and analysts. Statement in only tenths of a per cent is defective in that it implies correctness only in the unit column, and consequently an insufficient degree of accuracy. On the other hand, a statement in thousandths of a per cent implies a higher degree of accuracy than is possible with the limits of error obtaining in all but the most painstaking analytical work, and which is quite uncalled for in view of the variable composition of all rock masses from place to place, however great may be the apparent uniformity. It may be remarked that, in the course of compiling and examining thousands of rock analyses, I have found it to be true, almost without exception, that the few analyses given to thousandths of a per cent are remarkable chiefly for their poor quality, differing from the probable truth in some or all constituents by as much as one or more per cent. Statement in such ultra-refined terms may usually be regarded as evidence that the analyst has no just appreciation of the probable limits of error, or of the bases of accuracy in analytical work.

A final word must be said in regard to the recalculation of the analysis to an even 100 per cent. This is tantamount to the distribution of any errors over all the constituents, which is not justifiable, as has been said elsewhere. Furthermore, as Fresenius says, "such 'doctoring' of the analysis deprives other chemists of the power of judging of its accuracy." Whatever the results may be, and whether the summation be high or low, the figures for the various constituents must be given with their summation, as they are obtained from the analysis, if the whole is deemed to be worthy of publication at all. Any other procedure would give rise to reasonable suspicion as to the accuracy of the analysis, which can only be judged of by others if the actual figures are given.

PART II.

APPARATUS AND REAGENTS.

ALTHOUGH any well-equipped laboratory should have almost every piece of apparatus and nearly all the reagents which are necessary for the quantitative analysis of rocks, yet it may be convenient, especially for the independent worker, to give a list of those which should be available before an analysis is undertaken. Brief remarks will be made to explain certain points which it is especially useful for the inexperienced to know. The number of pieces of apparatus are those which it is deemed advisable to have on hand in order that the analysis may proceed without interruption for lack of the proper facilities. It is well to bear in mind when buying reagents that it is better to have a somewhat large stock on hand, as this can be tested for impurities once for all. This is especially true of sodium, potassium and calcium carbonates.

1. APPARATUS.

Balance.—A good balance is, of course, essential. It should be accurate and sensitive to one-tenth of a milligram. The bearings should be of agate, and the arm must be graduated for a rider. A case is necessary, and the usual accessories for specific-gravity work, and a support for weighing specimen tubes, should be provided. The set of weights (the larger ones preferably platinum plated) should run from 50 grams to 1 milligram, with riders. For suggestions as to the testing of the balance and weights, and the process of weighing, see

Fresenius. Before commencing an analysis the balance should be adjusted.

Platinum.—One lipped basin of about 300 c.c. capacity, 10 cm. across the top, and weighing about 100 grams.

Three crucibles, one of 40 c.c., and two of 30 c.c. Instead of one of the latter one of 20 c.c. will answer, while a 50-c.c. crucible also will not come amiss.

One Gooch crucible of 20 c.c. capacity and provided with cap for the bottom.

Each crucible, including the Gooch, must have its own cover, with which it is always to be weighed.

Two or three triangles of 5, 6 and 7 cm. along the side. It is well to make a series of parallel grooves with a file at one apex of each, to support the cover when the crucible is heated on its side (p. 105).

One spatula, about 10 cm. long and weighing about 10 grams.

One pair of platinum-tipped crucible tongs.

One piece of stout wire about 8 cm. long (p. 85).

Platinum-foil and blowpipe wire.

A small lipped platinum basin of 75 to 100 c.c., and weighing 10 to 15 grams, will be useful for the digestion of rock powder in acid, but a large platinum crucible will take its place. A large platinum basin, holding 900 to 1000 c.c., is a great desideratum in the determination of alkalies, but as this is very expensive it may be replaced by one of silver of the same capacity (weight about 300 grams), or if necessary by a porcelain one.

Especial attention should be devoted to keeping all platinum utensils bright, by the use of sea-sand, and also by the application of fused acid potassium sulphate when needed. The analytical results will not only be more accurate, but the life of the articles will be greatly prolonged. Hot platinum must never be touched by any other metal, and must be handled only with the platinum-tipped tongs.

Glass.—Two nests of lipped beakers, from 1000 c.c. to 50 c.c., with two or three extra of the smaller sizes. These are preferably of Jena glass.

Flasks of various sizes (flat-bottomed), preferably two each of 50, 100, 200, and 400 c.c. These also are better of Jena glass.

Several wash-bottles: two of about 500 c.c., one for general use, and one for boiling water in the iron determinations; three of 300 c.c., one of these reserved for ammonia in the determination of magnesia, another for alcohol in the determination of potash, and one for use with various dilute washing solutions. The jets should be attached by a bit of rubber tubing.

Measuring-flasks, with glass stoppers. One each of 1000 and 500 c.c., and three each of 250, 200 and 100 c.c.

Pipettes. Two each of 5 and 10 c.c.

Measuring-cylinders, lipped, unstoppered. One each of 10, 25, 100 and 500 c.c.

Burettes. Three of 50 c.c. each, divided to tenths of a c.c., with glass cocks. One of these is for permanganate solution, one for titanium and manganese solutions, and one for water.

Desiccators. Two or three of the usual form, with pipe-stem triangle. The bottom part is to be half filled with bits of glass tubing, and concentrated sulphuric acid poured in just sufficient to cover these. The acid should be frequently changed.*

Watch-glasses. Half a dozen each, 2, 2½, 3, 4, 5 and 6 inches. It will be found useful to perforate one or two of the larger ones by means of a mixture of hydrofluoric and sulphuric acids, this being retained in the center by a little ring of wax till a hole is eaten through. A pair of the 3-inch glasses is to be taken which weigh as nearly alike as possible, and the weights adjusted to equality by filing or grinding off the rim of the heavier the necessary amount.

Test-tubes. A few of several small to medium sizes.

Specimen tubes. A sufficient supply of the sizes, $6\times\frac{7}{8}$, $5\times\frac{5}{8}$ and $4\times\frac{1}{2}$ inches. Appropriate smooth corks should be provided for these.

Tubing. Sufficient of the usual sizes to make connections,

* Cf. Hillebrand, Am. Chem. Jour., XIV, 1892, p. 6.

etc. There should also be a supply of rather hard glass tubing, of an internal diameter of 6 mm., for the determination of water.

Rods. A supply of various thicknesses not over 3 mm. in diameter for stirrers. It is a common error with beginners to use too thick stirrers. A number of these should be prepared, varying in length from 5 to 10 inches. The ends are rounded by heat, and half an inch being bent at an angle of about 60° at one end. Two may be tipped with a bit of rubber tubing.

Funnels. Two or three each, 1½, 2, 2½, and 3 inches, with one or two larger, 4- and 5-inch ones. Care should be taken to select funnels whose conical angle is exactly 60°, especially for those of 3 inches and below, as this facilitates greatly the fitting of the filter. It will be well to fuse onto two each of the 2½- and 3-inch funnels suction-tubes of small bore, about 8 to 10 inches in length, and provided with a turn about half-way down. These may also be separate and attached by a bit of rubber tubing, though this method is less accurate and apt to lead to loss or contamination of the filtrate in inexpert hands.

A "carbon filter," of internal diameter of 1¼ inches, or to fit the Gooch crucible, provided with rubber tube to make the connection (Fresenius, I, p. 121).

A stout thick-walled Erlenmeyer flask of about 1000 c.c., with side tubulure for use with the Gooch crucible.

Calcium-chloride tubes and drying-cylinders for setting up the apparatus for the determination of CO_2.

Washing-bottles or cylinders for washing gases, preferably of Drexel's form. Two or three will suffice.

Apparatus for the generation of CO_2 and H_2S. Any one of the usual forms.

A pair of glasses with parallel sides, or a pair of Nessler tubes, for the determination of TiO_2.

Miscellaneous.—Evaporating-dishes, one or two each of 2½, 3½ and 4½ inches, preferably of Berlin porcelain.

Crucibles of Berlin porcelain. Two or three of small sizes.

One of about 2 inches diameter will answer as an air-bath for the evaporation of sulphuric acid in platinum crucibles.

A square white porcelain plate for use in the titration of iron.

Steel plate and ring (p. 50).

Diamond steel mortar (p. 55). This must be kept in a (cylindrical) wooden box, with close-fitting cover, to prevent rusting.

Agate mortar, about 3 inches in diameter, with pestle.

Glass box sieve for the rock powder (p. 55).

Best white silk bolting cloth, with about 25 meshes to the centimeter. Half a yard will be ample.

A steel plate or, preferably, polished granite slab, about 2×3 inches, for cooling crucibles.

Several two- and three-ring retort-stands. A glass tube, closed at one end, should be slipped over the upper part or the rod of these, above the normal position of the ring, to prevent any rust from falling into the vessel on the ring.

Two funnel-stands of wood.

One burette-stand, two arms.

Bunsen burners, and a blast-lamp, with bellows.*

Iron wire gauze, in 6-inch squares. This is preferable to asbestos board, though the latter may be used.

Water-baths, preferably with porcelain rings, and a copper air-bath, with thermometer reading to 200° C.

Aspirator or suction-pump.

Rubber tubing, a selection of sizes suitable for making connections, including some of narrow diameter for capping stirring-rods to be used as cleaners.

Rubber stoppers, perforated with one and two holes, for making wash-bottles, etc.

A hard rubber funnel, about 2 inches in diameter, if a platinum one is not available.

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* It may be of interest to state that, in my laboratory, where gas is not available, Berzelius and ordinary glass alcohol lamps are used for most purposes, a blast flame being obtained with a "Primus" kerosene lamp, and kerosene stoves serving for evaporations, etc.

A horn spoon for weighing out alkali carbonates, etc.

Filter-paper. Round cut filters should be used, the paper being of such quality as to leave only a negligible amount of ash. Schleicher and Schull's No. 590, and Baker's ashless "T" filter papers are excellent. Those of 5½, 7, 9 and 11 cm. are the most convenient sizes. While too large a filter is to be avoided as leading to an undue amount of wash-water, yet the filter must be large enough to allow all the precipitate to be brought on it. The appropriate size in each operation has been indicated throughout the descriptions.

2. Reagents.

All reagents should be the purest obtainable. In general these can be bought sufficiently pure, especially the strong acids and ammonia water. They should all be tested for impurities, according to the tests suggested by Fresenius* or Krauch,† and, if necessary, the salts are to be purified by recrystallization, etc. I must add my word of caution to that of Hillebrand in regard to the acceptance of C. P. reagents without proper tests, and especially as to the unreliability of some of those manufactured abroad, and sold under a guarantee of purity. I have found certain samples of these last worse than reagents with an ordinary "C. P." label, and, as Hillebrand says, "The 'guaranteed reagent' needs checking as much as any other." In the subjoined list the chemicals mentioned are supposed to be "chemically pure," and not of the ordinary commercial brands. A series of "Analyzed Chemicals" has recently been introduced by the Baker Chemical Company and by Merck, which appear to be reliable, so far as they have been tested in my experience with them. It is a wise precaution, however, to examine even these.

Hydrochloric acid.

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* Fresenius, Qual. Anal., pp. 52 ff., 1897; Quant. Anal., I, pp. 127 ff.,1904.

† Krauch, The Testing of Chemical Reagents, New York, 1902. Cf. Hillebrand, Bull. 176, p. 25; Bull. 305, p. 34.

Nitric acid.

Sulphuric acid.

The commercial acids may be used for generating CO_2, H_2S, etc.

Sulphurous acid. A solution of SO_2 in water is used for some reducing purposes.

Hydrofluoric acid, to be kept in ceresine bottles, not in gutta-percha.

Ammonia water. This should be fresh and must contain no ammonium carbonate (p. 66).

Ammonium chloride. This had better be resublimed.

Ammonium carbonate. The solution of this is made as needed (p. 148).

Ammonium oxalate. This had best be recrystallized, as it frequently contains calcium oxalate. The solution is to be made as needed (p. 127).

Ammonium nitrate. A solution containing 340 grams to the liter is used in the determination of P_2O_5, and the salt is sometimes used in the solid state.

Ammonium persulphate. The ordinary, pure salt serves for the colorimetric method for manganese. For the precipitation of this with the alumina a specially purified salt is necessary. Baker's "analyzed" reagent will usually answer, or the commercial salt may be purified by the method described by Hillebrand, (Bull. 305, p. 85, note). The reagent is used in the solid form.

Hydrogen-ammonium-sodium phosphate (microcosmic salt). The solution is to be made as needed.

Sodium acetate.

Sodium carbonate, dry, anhydrous.

Acid potassium carbonate.

These two are to be especially investigated as to impurities, since the quantity of them which is used for an analysis is very large. They are to be powdered and mixed in equal parts for the main fusion. Acid potassium carbonate is preferable to the normal carbonate, as it is not as deliquescent, and the water and carbonic acid are driven off readily by gentle heat-

ing (Penfield). The mixture of the two carbonates is preferable to the use of sodium carbonate alone, as it fuses at a considerably lower temperature than either carbonate alone, and is apparently equally effective as a flux, though Hillebrand (Bull. 305, p. 71) recommends the use of normal sodium carbonate alone. A considerable quantity of the mixture may be made and preserved in a glass-stoppered bottle.

Potassium pyrosulphate. This must be the fused salt, and should contain no water and as little free acid as possible. The sodium salt may also be used and is advocated by Hillebrand, but my preference is decidedly in favor of the potassium salt.

Calcium carbonate. The ordinary precipitated carbonate is not well adapted for the determination of alkalies, as it is too fine-grained and bulky, though it can be used. It is best made by precipitating a boiling solution of calcium chloride with ammonium carbonate, which renders the precipitate dense and relatively coarse-grained. The precipitate is to be thoroughly washed with hot water. The amount of alkalies can thus be reduced to very small amount, but for accurate work it is well to estimate them in 4 grams of the stock, so as to be able to apply the appropriate correction (p. 142). A suitably precipitated and very pure calcium carbonate is the Baker "analyzed" reagent.

Potassium nitrate.

Potassium chromate. The preparation of the standard solution of this is described on p. 181. 100 c c. is ample.

Potassium permanganate. A solution of strength appropriate for use in rock analysis is obtained by dissolving about 1 gram of the salt in 1 liter of water. One c.c. of this will correspond approximately to 0.0025 gram Fe_2O_3 or to 0.00225 gram FeO. The standardization may be effected by any of the methods given in Fresenius, the reagent which I prefer for this purpose being ammonium oxalate, which is easily obtained pure and dry. As the disappearance of color in this is at first very slow, it may be as well to note that 1 c.c. of the permanganate solution mentioned above will correspond to about

1 c.c. of a solution of 0.57 gram of crystallized ammonium oxalate dissolved in 250 c.c. of water, to which some sulphuric acid is added. The mean should be taken of at least three or four determinations on 25 or 50 c.c. of the oxalate solution. As equal amounts of permanganate are required to oxidize 1 molecule of ammonium oxalate (mol. wt. = 142) and 2 molecules of ferrous oxide (mol. wt. = 144), the weight of oxalate per cubic centimeter is to be multiplied by $\frac{144}{142}$ to give the equivalent per cubic centimeter in terms of ferrous oxide. This divided by 0.9 (or multiplied by 1.1111) will give the value per cubic centimeter in terms of Fe_2O_3. The solution should be kept in the dark, and it is well to restandardize it every few months.

Chloroplatinic acid. This is usually obtained as the hydrate $H_2PtCl_6+6H_2O$, which contains 37.66 per cent of platinum. A solution containing 0.1 gram of platinum per cubic centimeter is made by dissolving 1 ounce of this in 50 c.c. of water, filtering and washing the beaker and filter slightly, and diluting with water to 106 c.c.

Silver nitrate. A solution of this may be kept in a bulb for use in testing filtrates. A solution containing 2 or 3 grams to the liter is needed for the determination of manganese by the colorimetric method. A liter should be prepared.

Ammonium molybdate solution. This may be prepared by dissolving 100 grams of ammonium molybdate in 500 c.c. of water with the aid of heat, pouring it when cold into 500 c.c. of concentrated nitric acid.* The mixture is to be filtered after standing for a couple of days. It is kept in a well-stoppered bottle. On long standing so much of the molybdic acid may separate out as a yellow precipitate that the solution will give little or no precipitate when phosphoric anhydride is present, at least in the amounts found in igneous rocks.

Barium chloride. A solution of 10 grams in 100 c.c. of water will suffice.

* The precipitate which forms redissolves on the addition of all the ammonium molybdate solution.

Magnesia mixture. This may be made as suggested by Fresenius (Quant. Anal., I, p. 138, 1904) by dissolving 11 grams of crystallized magnesium chloride and 28 grams of ammonium chloride in 130 c.c. of water and adding 70 c.c. of dilute ammonia water (sp. gr. 0.96). An alternative method is that of dissolving 10 grams of crystallized magnesium sulphate and 20 grams of ammonium chloride in 80 c.c. of water, and adding 40 c.c. of ammonia water. In either case the solution must be allowed to stand for some days, and is then filtered.

Titanium standard solution. The preparation of this is described on p. 115.

Manganese standard solution. The preparation of this is described on p. 167.

Hydrogen peroxide. A commercial brand of this which is usually free from fluorine is known as "Dioxogen," and Merck also supplies a very pure article of ordinary strength, as well as a very pure and strong (30 per cent) "Perhydrol."

Zinc oxide. A little of this may be dissolved in ammonia water as needed for the rarely executed determination of fluorine.

Ferrous sulphide. This is used for the generation of hydrogen sulphide.

Marble. This is used for the generation of carbon dioxide.

Acetic acid. The ordinary acid of specific gravity 1.044 (33 per cent) will answer.

Alcohol. Ordinary 95 per cent ethyl alcohol may be diluted with water to a specific gravity of 0.86 for use in the determination of alkalies. If a hydrometer is not available, this may be attained approximately by mixing five volumes of the alcohol with one of water.

Alcohol, absolute. Ether. Small quantities of these will be ample for the determination of strontia.

Methyl orange. A weak solution of this in water is used.

Litmus paper. A little of both blue and red will be useful.

Asbestos. This must be of the anhydrous, hornblende variety, and not the fibrous serpentine (chrysotile) which is so often substituted for the other. The latter, being hydrous,

is not adapted for use in the Gooch filter. About 2 grams are to be boiled with dilute hydrochloric acid, thoroughly washed on a filter with hot water, and kept for use, mixed with 25 to 50 c.c. of water, in a small flask, which should be covered with a loose glass cap, the water being replaced as it evaporates.

Calcium chloride. The fused, granular salt is used for drying-tubes in the determination of CO_2.

Soda-lime. This is used in granular form for the absorption of CO_2. It should be renewed from time to time in the U-tube.

Water. It is, of course, understood that only pure, distilled water is to be used in quantitative analysis, and that this is referred to whenever this substance is mentioned throughout this book.

PART III.

THE SAMPLE.

1. Selection in the Field.

Since the object of the chemical analysis of rocks is to ascertain the chemical composition of a body of rock, it is of fundamental importance that the specimen selected for analysis, and the material analyzed, be truly representative of the mass under investigation. Otherwise the analysis, however accurate and complete it may be, will be misleading and useless for the end in view.

If, for instance, an igneous mass is not uniform in character, and the specimen is selected from some extreme phase of variation, it is obvious that an analysis of this will not give a just idea of the character of the mass as a whole. Again, in analyzing a diorite, for instance, the specimen may be so small or selected with so little care that it contains a larger proportion of hornblende, let us say, than the average of the mass; or the specimen of a quartz-porphyry may carry only a few of the abundant quartz phenocrysts and a disproportionate amount of groundmass. In these cases it is self-evident that the analysis made on such inadequate material, however skilfully it may be executed, cannot represent the true composition of the rock-mass. It is seen, therefore, that the proper selection of the material for analysis depends on two factors: the selection of the specimen in the field, and the amount of material taken for use in making the analysis.

While the selection in the field is quite distinct from the

laboratory processes, yet its importance is so vital to the proper analysis of rocks, that it demands some discussion here. This is the more called for since the petrologist will usually collect his own material, for analysis either by himself or by others, and, as has been said elsewhere, "the evidence is conclusive that the specimen analyzed has often been collected with no reference to this point, this fact greatly diminishing the value of the analytical work afterward expended on it." In selecting a representative specimen in the field attention must be paid to two points: the uniformity of the mass, especially in regard to mineral composition as well as to texture, and the freshness of the rock.

Uniformity of the Rock-mass.—If, as is probably true in the majority of cases, the igneous mass is sensibly uniform throughout its extent, specimens should be taken from several parts, when possible, in order to test the matter with the microscope. For an analysis representing the composition of such a uniform body of igneous rock, either portions of several specimens from different parts may be mixed, or the analysis may be made on a single specimen, which is considered to be representative of the whole in the judgment of the petrographer, both as decided on in the field and as confirmed by the microscope.

As to the former procedure it may be said that no decisive check of one's results will be possible in the future, and that it is by no means certain that a mixture of several specimens really represents the composition of the whole better than does a single specimen, which has been carefully selected with this object in view.

In all, or nearly all, cases therefore, it is by far the best plan to select a single specimen after due comparison with others from the same mass and consideration of its representative character. The specimen should be taken, if possible, from a mass of rock in place, and not from loose boulders or talus slopes, unless these are the only sources available and it is definitely known that they do come from the mass under investigation.

If the mass is not uniform, but is composed of portions of different characters, such as a composite dike or a stock with

marginal facies, representative specimens of the different facies should be collected and an analysis made of each, whether the differences be apparently only textural or those due to mineral composition. If in any way feasible, as close an estimate as the conditions allow should be made of the relative areas or volumes of each facies. While the possibility of doing this depends, to a large extent, on the chances of erosion and denudation, yet it is of such great importance in the investigation of certain theoretical questions of petrology that special endeavor should be made to arrive at the facts.

In any case, whether the mass be uniform or composed of several facies, the specimens should be taken from some definite locality, one which can be described or named so that it can be readily identified by others, and also one whose accessibility is not likely to be lost through building or other operations. Quarries naturally are especially favorable spots, as fresh specimens are easily obtained, and they are of such a permanent nature as to be readily identified, in most cases, by future investigators.

Freshness of the Rock.—The action of atmospheric agencies on rocks may vary from the changes to which Merrill * attaches the specific term "alteration," in which "the rock-mass as a whole retains its individuality," but is changed mineralogically, with the production of such minerals as chlorite, sericite, zeolites, serpentine, limonite, etc., to those embraced under what Merrill calls "weathering," "involving the destruction of the rock-mass," and its ultimate resolution into sands and clays. The mass resulting from such changes, either of alteration or weathering, can be analyzed by the same methods and with equal facility as can a perfectly fresh rock, but it is evident that the results will not represent the composition of the original magma or unaltered rock body.

While it is in general true that for purposes of analysis only specimens of fresh, unaltered or unweathered rock should be chosen, unless the study of such secondary changes is the object

* G. P. Merrill, Rocks, Rock-weathering and Soils, 1897, p. 174.

in view, yet it is at times somewhat difficult to decide whether a rock is fresh enough for analysis or not. In general it may be said that, for the study of igneous rocks, all weathered specimens are to be rejected, that is to say, those in which the rock-mass has been formally broken down. In the case of alteration, specimens should be rejected where the original color is decidedly changed, as where the rock is of a rusty brown through the abundant production of limonite, or green through that of chlorite. Specimens which effervesce with hydrochloric acid, either cold or on warming, or whose vesicles contain calcite or zeolites, are likewise to be shunned.

In rocks which appear megascopically to be quite fresh, the microscope may reveal the presence of secondary minerals, the products of alteration, as sericite, chlorite, serpentine or limonite. Although considerable latitude must be left to the judgment of the petrographer in deciding this matter, yet if such minerals are present to any considerable extent, the rock must be regarded as unfit for chemical analysis, unless fresh material is absolutely unattainable. This last state of affairs is especially apt to be true of the most basic rocks, such as picrites, peridotites and pyroxenites, which contain a large amount of the easily oxidizable ferrous iron, and of which few perfectly fresh occurrences are known or have been analyzed. For lack of better material, one must often make analyses on specimens of such rocks that are far from fresh, but the results of these, while not to be regarded as wholly satisfactory, may yet be of some service.

The results of alteration are usually most clearly shown in the analysis by the figures for H_2O or CO_2, or both. Where these are high the material analyzed must be considered as having been more or less altered, whether this appears in the description or not, with the exception of certain cases mentioned below. While it is impossible to state in exact figures the limits of allowable alteration, until the subject is further studied, it may be held provisionally that H_2O can go up to 2 or 3 per cent and CO_2 to $\frac{1}{2}$ or 1 per cent, without seriously affecting the value of the analysis. It must also be borne in mind that a rock can be more or less profoundly altered, and yet show comparatively

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low figures for these two constituents, though this is not often to be expected.

The exceptional cases just referred to consist of rocks composed in part of primary minerals which contain either hydroxyl (as muscovite and biotite), water of crystallization (analcite) or carbon dioxide (cancrinite). With rocks carrying analcite, which is the only zeolite that apparently may exist as a primary mineral, the H_2O may amount to 3 or 4 per cent, and yet the mass be to all appearances perfectly fresh, and often presumably so, as Pirsson has shown in the case of the monchiquites. Highly vitreous lavas, as perlites and tachylites, may contain several per cent of water and yet be perfectly fresh; while water often occurs as inclusions, as in the quartzes of many granites. Cancrinite-bearing rocks may have more than 1 per cent of CO_2 and yet be quite unaltered, as far as one may judge from the microscope, so that it is entirely possible, if not probable, that this mineral is a primary constituent in some cases. No well-established cases of the existence of calcite as an undoubtedly primary mineral are known as yet, though instances have been brought forward where its occurrence as such seems to be possible.

In discussing the subject of analyses of altered rocks we may advert to a phase of the matter which is of some importance. When a rock is not fresh it is sometimes assumed that the original composition can be arrived at by deducting the amounts of H_2O and CO_2 and calculating the remainder to 100 per cent. This assumption is quite unwarranted in the great majority of cases, since the processes of alteration are usually by no means simple and the result of the simple addition of the two substances mentioned. On the contrary, they are very complex and produce changes of greater or less magnitude in the proportions of some or all of the other constituents. These may be additive, as when calcite is deposited in rocks by means of percolating waters carrying calcium bicarbonate in solution, or they may be subtractive, as when kaolinization of a feldspar takes place with resultant loss of alkalies or lime. In any case it is almost universally true that the processes of rock

degeneration affect all or nearly all of the chemical constituents,* and that the assumption that such is not the case is quite unwarranted by the known facts.

2. Amount of Material.

As has been said above, the representative character of the specimen depends, after proper selection in the field supplemented by the use of the microscope, upon the amount of material which is taken for pulverization in preparation for the analysis. The weight of the sample which will adequately represent the average of the rock-mass varies with the texture of the rock, and especially with its granularity, that is, the size of its component mineral particles.

It may first be noted that at least 10 grams of rock powder must be available for the purpose of analysis, and this amount should be increased to 20 or 30 grams if the analysis is to be very complete, since the determination of some of the rarer constituents demands the use of two or more grams of powder. Indeed, it is always a wise precaution to have 20 or 30 grams on hand, in view of the possible necessity for the duplicate determination of some of the constituents, or even the making of a second complete analysis. In the case of many minerals and meteorites it is often impossible to obtain anything like this amount of material, and the analyst must be content with far smaller quantities, sometimes even less than a gram for the whole analysis. With rocks, on the other hand, there is usually an ample supply, so that the analyst has generally no reason for stinting himself. In this way a number of constituents can be easily determined in separate portions, which could only be accomplished by the use of longer and much more complex methods if it were necessary to determine them in a single portion.

The texture of rocks varies within such wide limits that it is difficult to give exact figures, and much must be left to the

* Cf. Merrill, op. cit., especially pp. 234 to 240.

judgment of the petrographer or analyst. Speaking generally, and almost without exception, the finer grained and less porphyritic the rock is the smaller will be the amount of material necessary to be representative.

Twenty or thirty grams of chips or fragments will be ample for very fine-grained, aphanitic or glassy rocks, as many basalts, trachytes, and obsidians, especially if non-porphyritic, or very finely so. With more coarsely granular rocks, such as granites, syenites and diorites, a larger quantity must be taken, depending on the coarseness of the grain. This amount may vary from 50 grams of a medium-grained rock to 100 or even more if the grain is coarse. In some cases, as in pegmatites, the grain may be so large that only a whole hand specimen, or even several pounds, will adequately represent the true composition. Very exceptionally the crystals may be of such gigantic size that the relative proportions of the various minerals must be estimated from a flat expcsure and corresponding portions of the several minerals weighed out and mixed. Fortunately this last will be necessary only in rare instances, as results obtained thus could be regarded as but approximations to the truth.

If the rock is porphyritic this feature involves the taking of a larger quantity than would be necessary if the grain of the whole were that of the ground-mass. If the phenocrysts are very small, only a few millimeters in diameter, and close together, as in many andesites and basalts, only 20 or 30 grams will be sufficient. As they get larger, and if more widely scattered, more must be taken, from 50 or 100 grams to larger quantities. With porphyritic rocks also care must be taken that brittle or loosely attached phenocrysts, as of feldspar or quartz, do not fall out, so as to yield a disproportionate amount of groundmass in the material for analysis.

3. Preparation of the Sample.

For the purpose of analysis it is necessary that the sample of rock be reduced to powder in order that it may be readily and completely attacked by the reagents used for its decomposition. To accomplish this one of three methods may be followed.

The first is that formerly advocated by Hillebrand* and employed in the laboratory of the United States Geological Survey. It consists in first crushing the rock fragments by means of a hardened steel hammer on a hardened steel plate. The plate used by Hillebrand is 4½ cm. thick and 10 cm. square, and the rock fragments are surrounded by a steel ring 2 cm. high and 6 cm. internal diameter to prevent the flying and loss of small rock fragments. After reduction in this way to very small particles and powder, the whole is ground down by hand in an agate mortar in small portions at a time.

The second method is that now employed in the laboratory of the Survey.† The rock, broken into small pieces, is crushed in a specially hardened steel mortar, of peculiar shape, somewhat resembling a "diamond" mortar, but with a tall cylinder and loosely fitting pestle. The crushing is done by the pestle alone, without the aid of a hammer. The material is then ground in an agate mortar by mechanical grinders, these having superseded hand grinding.

In the third method the rock is broken into small pieces, and these crushed in a steel mortar. The resultant mixture of small fragments and powder is sifted through a silk-gauze sieve, the part which does not pass through being once more crushed in the steel mortar and again sifted, and this operation repeated till only very small portion is left, which is pulverized by hand in an agate mortar.

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* Hillebrand, Bull. 176, p. 31.

† Hillebrand, Bull. 305, p. 46.

Of these methods it may be said that none is perfect, since all are open to rather serious objections, while, on the other hand, each possesses certain advantages over the other.

In favor of the first two are the facts that the preliminary rough crushing is quickly accomplished and with a minimum possibility of contamination by metallic iron, and that, the final pulverization being carried out in agate, the chance of contamination is here also very slight. Against the first it may be urged that in the preliminary crushing on the steel plate, which must necessarily be carried pretty far to prepare the material for grinding in an agate mortar, there is considerable flying of fragments, which the steel ring cannot wholly prevent, but which is obviated in the second method. This will be still more marked during the grinding in the agate mortar, in which it is almost impossible to avoid very notable loss, unless the material is already very finely crushed and there are no particles of any considerable size. The fragments thus lost may be of the same average composition as that of the rock, which will be true of aphanitic rocks or obsidians. But if the rock is medium- or coarse-grained, or contains phenocrysts, the chances are largely against this, since the more tough and resistant minerals, as pyroxene and hornblende, will be the most apt to fly off. They may be accompanied, it is true, by some adhering feldspar, but in less relative amount than in the rock itself. The result of this would be that the powder finally obtained would not quite correspond in composition to that of the rock, though the error thus introduced would probably be compensated for to a certain extent by the loss of fine dust during the grinding, which would contain more of the brittle quartz and feldspathic constituents.

Another, and very serious, objection against the first method is the great amount of time and labor involved in grinding down the crushed material in the agate mortar by hand, if the presence of coarse particles is to be avoided, as is essential for proper attack by the reagents used.

In my opinion the use of a mechanical grinder and the

long-continued grinding of the second method are to be deprecated. Apart from the cost and loss of time, the danger of contamination of the powder by oil or metal is always present, in spite of the shields and other safeguards introduced, and there is apt to be a very considerable loss of fine powder, as well as loss by flying of coarser particles as mentioned above. Furthermore, as mentioned by Hillebrand, "the abrasion of pestle and mortar becomes far more manifest with these machines than with hand grinding." The consequent introduction of silica is a serious matter, and may go far to offset the elaborate precautions recommended by Hillebrand for its determination in the analysis later. It is also to be noted that the reduction of the material to an extremely fine powder is not at all necessary for most determinations, except that of the alkalies, and that this, together with the long-continued grinding, are distinctly disadvantageous and introduce serious error in the determination of ferrous iron, as will be discussed later.

The advantages of the second method are the great saving of time over that needed for the first, and the avoidance of loss by flying fragments which is incident to the other, though it must be confessed that this is partially counterbalanced by a somewhat greater loss of fine dust. This will not, however, be very great or lead to serious error if the operation is conducted with care and in a place free from draughts, and anyway it seems to be unavoidable by either method. Another advantage is the comparatively very slight chance of oxidation of the ferrous iron, which has been shown to be a serious objection to the second method.

The most serious objection that can be brought against this method is the danger of contamination by particles of steel derived from the mortar. These cannot, of course, be removed by a magnet, as magnetite, pyrrhotite, and some pyroxenes, hornblendes, biotites and olivines are magnetic, and hence would also be extracted, and there are few rocks which do not contain some of these minerals.

While this objection is entitled to great weight and would

indeed be fatal if the contamination thus possibly introduced were of serious dimensions, yet experience goes to show that it is by no means as formidable as it appears at first sight. If a steel mortar of the best quality, and properly hardened, is selected, and there is no rubbing motion, the wear involved by crushing the material for any one analysis is so extremely small as to be entirely negligible. This is evident from the very slight total wear in such a mortar that has been in use for twelve years. Furthermore, although it would be expected that the small pieces of steel which may be torn off from the mortar would be caught in and not pass through the fine silk gauze, on account of their size and jaggedness, I have not found any present, although search has often been made for them with a lens. The practically total lack of abrasion in my agate mortar, also in use for twelve years, is good evidence that no appreciable amount of silica can be introduced from this source into any one analysis.

The objection which Hillebrand raises against the use of a silk sieve can scarcely be held to be of great moment. The danger of contamination by particles of silk, and hence error in the determination of the ferrous iron, is more theoretical than real. Only an almost infinitesimal weight of silk would pass into the rock powder, a milligram or so at the very most, and this would be distributed among twenty or more grams of rock powder, of which but half a gram is taken for the ferrous iron determination. It is certain that the reducing action of the small amount of organic matter thus introduced would be very much less than that necessary to decolorize a single drop of the permanganate solution, and hence would be entirely negligible, even for the most accurate work. As Hillebrand says, however, it is obvious that metal sieves should never be used, as there would be in this case almost certain contamination of serious importance.

While, after all, there is little to choose between the three methods, and while the fact that the second is now adopted by the chemists in Washington is a very strong point in its

favor, yet, taking all things into consideration, I have adopted in my own work, and can recommend, the third method, of which the details follow.

The "diamond" steel mortar is preferably of Plattner's form,* though one made of only two parts may also be used. In the mortar used by me the bottom of the depression is flat, though Penfield recommended that it be hemispherical, for greater ease in cleaning, and as was suggested in the first edition of this book. This, however, is more likely to give rise to a rubbing motion and consequent introduction of iron. The pestle should fit rather loosely into the cylinder, so as to prevent jamming by heating through friction or by the rock particles and powder. The sieve consists of a cylindrical glass box, which may be 3.5 cm. deep, 7.5 cm. internal diameter and the walls about 2 mm. thick. With this is a brass ring, 1 cm. in height, and of such a diameter as to fit snugly over the mouth of the box. The gauze used is the best silk bolting-cloth, with about 25 meshes to a centimeter. An agate mortar about 7.5 cm. in diameter will be found a convenient size.

The whole amount of the sample which is deemed to be representative of the rock-mass is reduced to small fragments, either on a steel plate with a ring, as in the first method, or if the amount of material is small, by breaking up with a hardened hammer on the top of the steel pestle which is placed in position in the mortar. Care must be taken in either case to avoid the flying off of fragments.† If the pieces of rock are broken on the pestle-head they can be held in the dry fingers and cracked by a sharp, quick blow, and the pieces so obtained cracked again. The largest of the fragments finally obtained must be small enough to drop easily into the mortar, and all of

* Fresenius, I, p. 52, Fig. 25.

† Wrapping the rock in paper for the first breaking up, as is sometimes done, is not to be to be recommended, as it is almost impossible to free the fragments entirely from adhering paper, and the considerable organic matter thus introduced will lead to serious error, especially in the determinations of FeO and H_2O.

them, with any resulting small grains and powder, are placed on a clean sheet of white, glazed paper.

One of the small fragments of rock is then placed in the steel mortar, which rests on a firm, solid support, preferably a large block of wood, and is partially crushed by a dozen or so sharp blows of a light (one-half pound) hammer. The pestle is removed and placed on the sheet of paper, and the contents of the mortar dropped into the glass box, from which the gauze and brass ring have been removed. A few gentle taps of the base of the mortar against the cylindrical portion assist in removing the last portions of adhering powder. It is well to break up any coherent lumps of fine powder in the glass box by gentle pressure with the pestle, as this will aid materially in the subsequent sifting.

It is absolutely essential, as pointed out by Hillebrand and as confirmed by my own experience, that there should be no rubbing or grinding motion during the crushing. The pestle and cylinder should be held firmly in the fingers of the left hand, so that there may be no rotary motion, and the blows of the hammer should be strictly vertical. Any grinding of the pestle against the sides of the cylinder or rotation on the rock powder will surely introduce some iron through the wearing of the surface.

The whole of the fragments and powder resulting from the first crushing are to be thus passed through the mortar and placed in the box. The mortar should not be filled more than a third full at a time, and it is not necessary, nor possible, to crush all of the rock to a fine powder at this stage. Care should be taken that the cylinder is placed vertically in the base before any fresh material is placed in it, and that the pestle is also inserted in a strictly vertical direction. Lack of attention to these points gives rise to the danger of small shavings or chips of steel being cut off and falling into the rock powder.

When all the sample taken has been thus partially pulverized and placed in the glass box, a piece of the silk gauze, about 10 or 12 cm. square, is stretched over its mouth and held firmly in

place by the brass ring which is slipped over it. The sieve is then held upside down over another sheet of white, glazed paper,* about 300 by 400 cm. (12 × 16 inches), a short distance above it, and gently shaken from side to side. This operation should be conducted as gently as is consistent with proper efficiency, and in a place free from draughts, so as to avoid undue loss of dust.

When no more powder falls through, the brass ring and the gauze are removed, and the contents of the box poured out on the first sheet of paper. The whole process of crushing in the steel mortar is then gone through with on this material, exactly as before, and it is again sifted. The residue from the second sifting is again treated, and if necessary the process is repeated till only a small amount of powder is left in the glass box, too coarse to pass through the gauze. This may then be ground down by hand in the agate mortar in small portions at a time, the different portions as they are ground being scattered over different parts of the low heap of powder on the sheet of paper. Unless the amount of material to be crushed is very large, or the rock extremely tough, three or four successive crushings will be all that will be needed. The final grinding of the last small lot of powder should never be omitted, as this consists of the tougher minerals of the rock, and if it were thrown away, the correspondence between the sample and the rock would be incomplete.

When the whole is thus brought upon the large sheet of paper, the powder is very thoroughly mixed. This is best accomplished by tilting up successively the ends and the sides of the paper until the mass is in the center. One end of the sheet is then raised gently until the heap of powder is lifted and turned over and slid toward the other end. It is essential to proper mixing that the mass of powder should not only slide down, but that it should actually be turned over. This is repeated many times, not only from end to end but from side to side, with an occasional oblique roll. A platinum spatula may also be used to mix the powder, care being taken that none of the paper surface be

* The sheets used by botanists for herbaria will be found convenient.

rubbed off, but the process described above is to be preferred. When it is considered that the powder is thoroughly mixed, it is not an undue precaution to roll it over in different directions several times more. The powder may also be mixed by putting it again in the box and sifting it through a somewhat coarser gauze.

After thorough mixing, the powder is poured into a specimen tube. For amounts of 20 to 30 grams one $6\times\frac{7}{8}$ or $5\times\frac{5}{8}$ inches will answer, while one of $4\times\frac{1}{2}$ inches will hold about 10 grams of rock powder. The tube used must be carefully cleaned, inside and out, by washing with distilled water, and thoroughly dried. This is best accomplished by the application of a gentle heat, the moist air being at the same time sucked out through a piece of glass tubing attached to a suction-pump. The tube must be perfectly cool before the powder is introduced, and is closed with a smooth, well-fitting cork, on the top of which the number of the specimen is written in ink.

If the amount of rock to be taken is so large as to render crushing in small portions at a time in the steel mortar very laborious, that is, if it is 100 or more grams, and especially if a whole hand specimen or several pounds need be taken, it is best to crush the whole rather fine on an iron plate with a surrounding ring, and take out a portion by quartering. For this the crushed mass is poured on a large sheet of paper and well mixed. With a clean steel spatula portions are removed from different parts of the mass, care being taken that they do not include undue proportions of either the coarse fragments or the more finely powdered material. These selected portions, amounting to about 50 grams, are placed on another sheet of paper, and the operation of crushing in the steel mortar conducted on this, exactly as described above.

In order to avoid possibility of rusting, the steel mortar should be cleaned, a stiff brush and a dry cloth being used, as soon as possible after the preparation of the samples, and placed in a tightly closed wooden box. The bolting cloth may be used many times, but it must be very thoroughly dusted free from

any trace of rock powder, after each operation. For the most accurate work a fresh piece is to be taken.

It is of the utmost importance to note that the whole of the sample which is prepared for the steel mortar, either the chips if the amount of material be small or that obtained by quartering if it be large, should be pulverized and passed through the sieve or ground in the agate mortar. If it is only partially pulverized and the last portions rejected, it is clear that the powder obtained will not represent the average composition of the rock. The rock-forming minerals differ widely in brittleness, so that the portions pulverized first will have a content higher than the average in particles of the more easily pulverizable minerals, as quartz, feldspar and feldspathoids, while the last portions will be especially rich in the tougher minerals, pyroxene, hornblende and the micas.* The micas, above all, are difficult to pulverize completely either in the steel or agate mortar, on account of their ready cleavage and flexibility, but the thinness of their flakes renders these quite easy of attack by the reagents used. If they are present in any quantity it is necessary to see that the flakes are well distributed.

The analysis should always be carried out on air-dry powder, as specially dried rock powder invariably reabsorbs some or all of the lost moisture by exposure to the air during the weighing and whenever the tube is opened, or even in time if it be closed.† This absorption of water is the greater the finer the powder, and the amount of water thus absorbed has been shown by Day and Allen ‡ to be of the same order of magnitude as that of the "hygroscopic" water observed in the analyses of feldspars and many rocks free from hydrated minerals.

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* Some data are given by I. A. Williams, Amer. Geol., XXV, 1905, p. 38.

† Cf. Hillebrand, Bull. 176, p. 32; Bull. 305, p. 54.

‡ Publ. Carnegie Inst., No. 31, 1905, p. 57; and Am. J. Sci., XIX, 1905, p. 127.

PART IV.

METHODS.

1. Preliminary Observations.

To ensure satisfactory results the analyst must be scrupulously particular about the freedom of the laboratory from dust and the cleanliness of his apparatus. No matter how clean the laboratory may be, all vessels whose contents must stand for more than a short time, and especially overnight, are to be kept covered to avoid the entrance of dust. These are to be labelled with a paper containing the number of the specimen and the constituent to be determined laid on the cover. In prolonged evaporations it is well to hold a large pane of glass or a Meyers evaporating funnel at some distance above the liquid, which may be done with a clamp and support devoted to this purpose.

It is well to make it a rule to wash and wipe dry all glassware and other apparatus as soon as possible after use. Soiled vessels will then not accumulate, nor will there be danger that they be put away and used by mistake for clean ones. A clean beaker is to be used to collect a filtrate, even if this is to be rejected, to permit the recovery of the precipitate in case part of it passes through the filter or the latter breaks. Before using a clean beaker or flask, it is best to rinse it out with a little water, and in volumetric or colorimetric work the burette should always be rinsed out with a little of the solution before filling it, even if it is apparently dry. If it is moist, the drops of water present will dilute, and hence change the strength of, the standard solution.

If a good grade of filter-paper be used, such as those recommended elsewhere, the weight of filter ash may be neglected in the calculations, as it will fall within the other limits of error. The only general exception would be in the case of the precipitate by ammonia, for alumina, etc., when three or more 11-cm. filters are used and ignited. The combined weight of their ashes may not be negligible in accurate work, and should be deducted from the weight of the ignited precipitate.

In regard to the weight of the portions which it is recommended to take for the various determinations, it should be borne in mind that they are intended for the great majority of rocks, and that in exceptional cases they are to be departed from according to the judgment of the analyst. For instance, in the analysis of iron ores, if a gram be taken for the main portion the bulk of the voluminous precipitate of ferric hydroxide will be so great that it cannot all be brought on one filter, and possibly not on two. In such cases, therefore, only half a gram of material need be taken, even though extra care must be paid to the determination of other constituents. On the other hand, for the determination of alkalies in peridotites and other rocks in which their amount is extremely small, a whole gram of powder should be taken, instead of the half gram which is usually sufficient.

The beginner should take full notes during the progress of the analysis, until the various methods become familiar, and even then all occurrences or manifestations out of the ordinary are to be noted and not left to memory. The details of all the calculations are to be recorded in the note-book for future reference. It may sometimes happen that an apparent analytical error or an unsatisfactory summation is merely due to a slip in arithmetic, and a reexamination of the recorded weights and calculations may obviate the necessity of a duplicate analysis.

In rock analysis a preliminary qualitative examination is seldom, if ever, necessary. The microscope will often serve the purpose. But if not, and if the presence of some unusual substance is suspected, it is better, as Hillebrand remarks, to assume its presence and conduct the quantitative analysis on this

assumption. This will be time saved in the end, even if the result is merely to prove the absence of the suspected body, which in itself will be a fact of some interest. One should always test by qualitative methods the character of the weighed precipitate in such cases, to see whether it is really the substance in question or not.

Finally, before beginning an analysis the student should see that the balance is correctly adjusted, and that all the necessary apparatus and reagents are at hand, so that the work may proceed without interruption. It will be well to read the whole of the description of each of the various methods before beginning their execution, as some information may be given at the end which is essential to the proper performance. Thus, in the determination of combined water, if the rock which is being analyzed contains haüyne or sodalite, and the whole description of the method has not been read, the student may be unaware of the necessity for binding the chlorine or sulphuric anhydride with lime, and so obtain erroneous results.

2. General Course of Analysis.

Before beginning the detailed description of the methods for determining the various constituents, it will be advisable to state in a concise way what the course of analysis is, in what separate portions the different constituents are determined, and the plan of separation, in order to obtain a general survey, and so that the details may be considered later with greater intelligence and knowledge of their relations to the whole analysis. In this summary, if there are several alternative methods which are described subsequently, only that one will be mentioned which especially recommends itself for the use of students, and which, in general, I have adopted for my own work.

a. In a portion of 1 gram, silica, alumina, total iron as ferric oxide, manganese, lime, strontia, magnesia and titanium dioxide are determined. The powder is fused with five times its weight of mixed sodium and potassium carbonates, the melt

dissolved in hydrochloric acid and evaporated to dryness, thus rendering the silica insoluble. The silica is filtered off and in the filtrate alumina, ferric oxide, titanium dioxide and phosphoric anhydride are precipitated by ammonia water, with or without the addition of ammonium persulphate. After filtration the precipitate is dissolved in nitric acid and reprecipitated by ammonia, and this repeated if there is much magnesia present. The precipitate is ignited and weighed, and then brought into solution by fusion with potassium pyrosulphate. The melt is dissolved in water, the ferric iron reduced by hydrogen sulphide, the excess of this boiled off, and the total iron determined by titration with potassium permanganate. Titanium dioxide is determined in the same liquid by the colorimetric method, which consists in comparing the intensity of color of a known volume of the titrated fluid after oxidation by hydrogen peroxide, with that of a standard solution of titanium colored in the same way.

The filtrate from the ammonia precipitate is precipitated with ammonium oxalate, the precipitate of calcium oxalate dissolved and reprecipitated, and the lime determined as such by ignition of the oxalate.

Strontia may be determined in the weighed lime, obtained as above, by solution in nitric acid, evaporation to dryness, solution of the calcium nitrate by a mixture of ether and absolute alcohol, solution of the insoluble strontium nitrate in water and precipitation as sulphate after addition of alcohol.

In the filtrate from the calcium oxalate the magnesia is determined by precipitation as ammonium-magnesium phosphate, which, after solution and reprecipitation, is ignited and the magnesia weighed as pyrophosphate. The filtrate from this last operation is rejected.

b. Ferrous oxide is determined in a portion of powder of half a gram by solution in a mixture of hydrofluoric and sulphuric acids at a boiling heat, the operation being conducted in a well-closed platinum crucible. The contents of the crucible are transferred to water and titrated with potassium permanganate.

c. A portion of half a gram of specially ground powder serves for the determination of the alkalies, which is effected by the Lawrence Smith method. The powder is intimately mixed with ammonium chloride and calcium carbonate, and fused. After thorough leaching the filtrate is precipitated with ammonium carbonate, and the filtrate from this is evaporated to dryness. The ammonium chloride is driven off from the alkali chlorides by cautious heating, and the mixed chlorides of sodium and potassium weighed. The potassium is separated by the use of hydrochloroplatinic acid, and the potassium weighed as platinichloride, the soda being determined by difference from the weight of the mixed chlorides.

d. In a portion of ½ to 1 gram, combined water is to be determined by Penfield's method. The powder is ignited in a dry glass tube sealed at one end, and the water driven to the cool portion of the tube, the end containing the powder drawn off, and the water weighed in the remaining portion. The amount of hygroscopic water is deducted.

e. In a portion of about 1 gram, hygroscopic water is determined by heating at a temperature of 110°. This portion may also be used afterward for the determination of other constituents, as P_2O_5, or S, ZrO_2, and BaO.

f. In a portion of about 1 gram, phosphoric anhydride is determined by digestion with nitric and hydrofluoric acids, removal of silica by evaporation, and subsequent precipitation as ammonium phosphomolybdate. The precipitate of this substance is dissolved in ammonia water, the phosphorus is thrown down by magnesia mixture as ammonium-magnesium phosphate, and weighed as magnesium pyrophosphate.

g. Manganese is determined in a portion of 1 gram, the rock powder being broken up by heating with sulphuric and hydrofluoric acids, the excess of the latter being driven off. To the filtrate a solution of silver nitrate and some ammonium pyrosulphate are added and the liquid heated, the manganese being oxidized to permanganate. The manganese in this is

then determined colorimetrically, by comparison with a standard solution of manganous sulphate similarly treated.

h. In a portion of 1 gram, total sulphur, zirconia and baryta may be determined. The rock powder is fused with alkali carbonates, and the melt leached with water. After acidification of the filtrate with hydrochloric acid the sulphur is precipitated and weighed as barium sulphate. The zirconia is dissolved out of the residue insoluble in water by very dilute sulphuric acid, and, after addition of hydrogen peroxide, is thrown down and weighed as basic phosphate by the addition of sodium phosphate. The barium remains as sulphate after solution of the zirconia. It is brought into solution by fusion with alkali carbonate, which converts it into carbonate, leaching out the melt with hot water, and solution of the residue in hydrochloric acid. It is precipitated as sulphate, in which form it is weighed.

i. Sulphuric anhydride is determined in a portion of about 1 gram by digestion with hydrochloric acid and precipitation as barium sulphate.

j. For chlorine a portion of 1 gram is digested with chlorine-free nitric acid, and the chlorine precipitated in the filtrate by silver nitrate.

k. Fluorine is determined in a portion of 2 grams by fusion with alkali carbonates, leaching with water, precipitation of the filtrate with ammonium carbonate, the filtrate from which is precipitated with an ammoniacal solution of zinc oxide. In the filtrate from this a mixture of calcium carbonate and fluoride is precipitated by calcium chloride, and the calcium carbonate dissolved out by acetic acid, leaving the calcium fluoride, in which form the fluorine is weighed.

l. A portion of from 2 to 5 grams is used for the determination of carbon dioxide. The rock powder is decomposed by hydrochloric acid in a small flask, and the carbon dioxide absorbed in a weighed U-tube containing soda-lime, precautions being taken to keep the apparatus full of a current of air free from carbon dioxide, and to properly dry and purify the gas given off from the rock.

m. For chromium a gram of rock powder will suffice, though 2 grams are preferable. After fusion with alkali carbonate and a little potassium nitrate, and subsequent leaching with water, the chromium is determined as chromate in the filtrate, if necessary after concentration by evaporation, by a colorimetric comparison of a known volume of the solution with a standard solution of potassium chromate.

n. For copper and nickel a portion of 2 grams is decomposed by a mixture of nitric and hydrofluoric acids, filtered, evaporated to dryness, the residue taken up with dilute hydrochloric acid, and the copper precipitated in the acid filtrate by H_2S, and weighed as CuO. The filtrate from this is boiled to drive off H_2S, precipitated with ammonia water, and manganese and nickel precipitated in the filtrate with ammonium sulphide. The manganese is extracted from the precipitate by dilute acid, and the nickel weighed as oxide.

3. Chief Sources of Error.

It may be found useful by the student to have pointed out those portions of the various methods where error is liable to occur, and in regard to which especial care should be taken. The list is not intended to be complete, and general sources of error, such as incomplete washing or entrance of dust, are omitted. Certain small corrections are also not mentioned, as being refinements beyond the needs of the average student. Hillebrand's book abounds in these, and it is therefore especially valuable to the practised analyst.

Silica.—Hillebrand* has shown that a double evaporation to approximate dryness yields more accurate results than the older and more usual method of a single evaporation and subsequent heating at 110° or 120°, by which a notable amount of silica passes into solution. By the first method practically all the silica is rendered insoluble, only a minute amount being found in

* Hillebrand, Bull. 176, p. 52; Bull. 305, p. 75.

the alumina precipitate. Prolonged heating at 110° or 120° is apt to increase the amount of impurity in the silica, and also allow more silica to be dissolved in the treatment with HCl. The silica thus dissolved is shown by Hillebrand to be not wholly precipitated along with alumina, etc., and he also shows that silica is not perfectly insoluble in melting potassium pyrosulphate. Blasting of the silica for at least twenty minutes is essential for the complete expulsion of water. The weight of the silica must always be checked by evaporation with hydrofluoric and sulphuric acids, whatever the rock may be, as it is never pure.

Alumina.—In precipitating this, if ammonium salts are not present in sufficient amount, some magnesia falls down with the alumina, thus increasing the apparent quantity of this and diminishing that of magnesia by the same amount. This is an extremely frequent source of error, especially in basic rocks containing considerable magnesia, and it should be carefully guarded against by the analyst. It has undoubtedly caused more trouble and has rendered worthless more rock and mineral analyses, than any other single special source of error, and possibly more than all others combined.

The analyst must, therefore, be sure of an abundance of ammonium salts (preferably chloride), in the liquid, and also make it a rule to dissolve the first precipitate and reprecipitate with ammonia once at least, and twice or thrice in basic rocks, if ammonia alone or only once if sodium acetate, has been employed for the first precipitation.

If the ammonia water used is not fresh and contains ammonium carbonate, some calcium carbonate will be thrown down with the alumina, and will, of course, increase its amount and diminish that of the lime of the rock to the same extent. In case of doubt the ammonia water should be tested with $CaCl_2$ before using, and if a precipitate is formed it should be rejected, or redistilled from quick lime.

Another precaution to be observed in regard to the use of ammonia water is that if the bottle has been in use for hold-

ing it for a long time, the interior is apt to be acted on by the alkaline liquid, with the result that, besides impurities going into solution, the liquid will contain small flakes of silica or partially decomposed glass, which will increase the apparent weight of alumina or appear with the extra silica separated later. In such cases a new bottle must be taken for holding the ammonia water. Hillebrand (Bull. 305, p. 35) recommends that the ammonia stock bottles be coated on the inside with ceresine to prevent this.

Prolonged boiling or standing of the liquid after addition of the ammonia is to be avoided, as this will not only render the precipitate slimy and hard to filter, but will also lead to the precipitation of some lime through the action of the atmospheric carbon dioxide.

The final precipitate by ammonia must be washed absolutely free of all traces of chlorine, since any of this, if present, will combine with the aluminum and iron on ignition, forming aluminum and ferric chlorides, which will volatilize and lead to loss of alumina and ferric oxide. For this reason the first and second precipitates should be dissolved in nitric acid, rather than in hydrochloric, thus rendering complete washing from chlorine far more easy (Penfield).

If the basic acetate method is employed for the first precipitation, regard must be had to the probability of some alumina and ferric oxide not being precipitated and passing through with the filtrate, unless the conditions as to acidity and the amount of free acetic acid are very exactly adjusted. The only way to guard against this is by care and strict attention to the conditions as laid down in the description of the method. But even under favorable circumstances, and in the hands of experienced analysts, a little alumina especially is liable to be found in the filtrate. This should always be recovered before precipitation of the manganous oxide, though this precaution is frequently neglected, apparently through ignorance of its necessity. The amount of the error is usually not very large, but may reach as high as 2 per cent of the rock, judging from some analyses

with such abnormally, and otherwise inexplicably, high percentages of MnO. As, however, it affects to a very notable extent the figure for the highly important alumina, the basic acetate method should not be used by the inexperienced student, and had best be avoided altogether in rock analysis, or if adopted should be carried out with the greatest caution. It may be noted that, chiefly on account of this source of error, Hillebrand * prefers precipitation by ammonia in many cases, and that Jannasch rejects the basic acetate method altogether.

Alumina is always determined by difference, and therefore all the errors are thrown upon it which may be involved in the determination of Fe_2O_3, TiO_2, ZrO_2, P_2O_5, Cr_2O_3 and V_2O_3. As Hillebrand says, however, these may balance, and anyway there seems to be at present no escape from this mode of procedure, since as yet no satisfactory method has been devised for its separation and direct determination, at least without the expenditure of an inordinate amount of time. This fact, as well as the numerous possible sources of error noted above and the importance of alumina from the chemical and mineralogical points of view in the application of the analysis, emphasize the necessity for extreme care in the separate determination of the various constituents weighed with it.

The method of separation from iron which is sometimes employed in Europe, by fusion of the ignited precipitate with sodium hydroxide in a silver crucible, should never be used, as it is open to very grave objections.†

Ferric Oxide.—A not infrequent source of error in the determination of this is incomplete reduction to the ferrous condition before titration with permanganate. The current of H_2S, which is the best reducing agent and which should always be used, must therefore be allowed to pass for at least ten or fifteen minutes, and until considerable sulphur has separated out.

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* Hillebrand, Bull. 176, p. 55; Bull. 305, pp. 83, 96; Jannasch, p. 319; and cf. the remarks of Fresenius, I, p. 647.

† Cf. Hillebrand, Bull. 176, p. 59; Bull. 305, p. 94.

Care should also be taken that the air in the flask, in which the expulsion of the excess of H_2S takes place by boiling, be replaced by CO_2, and that the boiling be not long continued carried out to a very small volume of liquid, when the strong sulphuric acid is liable to oxidize part of the ferrous iron.

Zinc is to be avoided as a reducing agent, partly because perfectly pure and iron-free zinc is difficult to procure, partly because of the difficulty of ascertaining when reduction is complete, and still more on account of the reducing effect of nascent hydrogen on TiO_2, which is always present, and on V_2O_5, the lower oxides of which would affect the permanganate and thus appear as ferric oxide.

Ferrous Oxide.—Hillebrand * has discussed the reliability of the Mitscherlich method by decomposition by sulphuric acid in a sealed tube, which is widely adopted in Europe, and shown that it tends to too high values, owing to the oxidizing effect of ferric sulphate on the pyrite present in the rock under the conditions of decomposition, and the consequent reduction of part of the ferric iron of the rock to the ferrous condition. This is especially marked in basic rocks, which are high in iron, and which are those where pyrite is most frequently met with. Even if sulphides are not present, it offers no advantages, besides being very troublesome, taking much time, and subject to uncertainty as to the complete decomposition of the rock powder, and the possible solution of the glass of the tube. This method should therefore be abandoned, and replaced by that of decomposition by hydrofluoric and sulphuric acids in an atmosphere of steam, or of steam and carbon dioxide.

In this latter there is liability to error in the hands of the inexperienced through partial oxidation of the ferrous iron. This is, however, very largely a matter of manipulation, and should not noticeably affect the results after some practice. It is always the wisest plan in particular analyses, when possible, to make duplicate determinations of ferrous oxide.

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* Hillebrand, Bull. 176, p. 88; Bull. 305, p. 131.

Since a solution of potassium permanganate, though quite stable, is liable to suffer decomposition on long standing, care should be taken, in the determination of both ferric and ferrous oxides, that its assumed strength is unchanged, the tendency being to too high values for iron owing to weakening of the solution. The solution should therefore be standardized from time to time, say every two or three months. This is a precaution which is not always sufficiently well observed.

Magnesia.—The chief source of error here is that already mentioned in connection with alumina, namely, the tendency to partial precipitation as hydroxide by ammonia along with alumina. This must be prevented by the presence of sufficient ammonium salts and repeated precipitations, as already described.

An error of less magnitude and importance, but which should be avoided, is that involved in the precipitation of the ammonium-magnesium phosphate. If there be present excess of ammonia, ammonium salts and precipitant, the ammonium-magnesium phosphate, and hence the magnesium pyrophosphate, will not be normal in composition, owing to the presence of extra P_2O_5, as pointed out by Neubauer * and by Gooch and Austin.† This must be corrected by solution of the first precipitate and reprecipitation from the acid solution by a slight excess of ammonia. This error will not affect the other constituents, but will raise the figures for MgO only, and hence the summation of the analysis.

The magnesia will be low if the precipitate of calcium oxalate is not precipitated twice, as mentioned below.

If manganese is not precipitated with the alumina, and is not separated subsequently as sulphide, part of it will be thrown down with the lime and part with the magnesia, causing plus errors, that for the magnesia being the greater. As the amount of manganese in most rocks is very small, these errors will

* Neubauer, Zeits. Angew. Chemie, 1896, 435.

† Gooch and Austin, Am. J. Sci., VII, p. 187, 1899.

seldom be serious or notable, but they are avoidable by the procedure outlined subsequently.

Lime.—The only serious source of error in regard to this is the possible presence of ammonium carbonate in the ammonia water used for precipitating the alumina, etc., which will render the apparent amount of CaO too low, as has been already described.

The first precipitate of calcium oxalate invariably contains some soda and magnesia, and it should therefore be dissolved and reprecipitated.

Alkalies.—The Lawrence Smith method is so much superior to all others, both as to accuracy and saving of time, that it should always be employed. Its only inherent serious source of error lies in the fact that the calcium carbonate usually contains a very small amount of alkalies, chiefly sodium salts. But the amount of these can be determined once for all in a weighed portion of the stock of calcium carbonate, and the small constant correction is easily and safely applied. If the carbonate is well prepared and thoroughly washed, the error involved by neglect of applying this correction will seldom be serious.

The other methods of decomposition, involving the separation of alumina, iron oxides, lime and magnesia by the usual methods, introduce a large element of uncertainty through impurities in the reagents used and through the possibility of the introduction of alkalies from the glass vessels. They are also far more laborious and much longer in point of time.

It must be mentioned that in a recently published * comparison of the Lawrence Smith with the usual European method for determining alkalies, Dittrich comes to the conclusion that the one is as accurate as the other, and favors the use of the former on account of its greater expedition. It may well be doubted, however, if in the hands of less expert analysts the second method would compare as favorably as it does according to the figures given by him. But even if so, the point of labor

* M. Dittrich, Neues Jahrbuch, 1903, II, p. 80.

and time saved should certainly decide analysts in favor of the former.

Titanium Dioxide.—There are few sources of error of serious importance in the determination of this by the colorimetric method, which is the one to be employed in almost every case. If the hydrogen peroxide contains fluorine, as occasionally happens, the results will be too low (Hillebrand), and this reagent should therefore be tested for this impurity before use.

It is also highly important for obtaining correct results that the eye of the analyst be trained in the color comparisons. The beginner, therefore, should make many practice tests with known and varying amounts of standard titanium solution, until he has confidence in his judgment. With practice the method is capable of very exact and concordant results.

Use of the old method of determining TiO_2 by prolonged boiling in a dilute acid solution with SO_2 is to be discouraged. Precipitation of metatitanic acid is by no means complete in all cases, and that which is precipitated is almost always contaminated by alumina and ferric oxide. It is also extremely liable to adhere very firmly to the sides of the beaker, whence it is removed with great difficulty. After thorough trial, with various modifications, I have rejected this method entirely.

A drop or two of H_2SO_4 must always be added to the hydrofluoric acid before evaporation of the silica with this, as otherwise the whole of the titanium present in the silica will not be retained but will be partially vaporized as fluoride. The assumption is sometimes made that the residue from evaporation of the silica represents the amount of TiO_2 in the rock. This is quite unwarranted, as the residue contains only part of the TiO_2, as well as Al_2O_3, Fe_2O_3, P_2O_5, etc.

Phosphoric Anhydride.—The liability to the formation of ammonium-magnesium phosphate of abnormal composition through excess of ammonium salts or magnesia mixture, similar to that spoken of under magnesia, also affects this constituent. But for the small quantities of this substance ordinarily found in rocks this error is of no great moment.

Manganous Oxide.—The error involved in the separation of this by the basic acetate method has already been discussed (p. 67), so that it need not be enlarged on here. It may also be mentioned that the gravimetric determination of manganese, after separation from the alumina filtrate will add at least a day to the time required for the analysis, and its non-determination will add slightly to the apparent amounts of lime and magnesia. The colorimetric method recommended for its determination is very accurate for the small amounts found in rocks, and no serious sources of error are involved.

Water.—The error involved in the determination of combined water by the loss on ignition, through the oxidation of ferrous iron or the expulsion of other volatile substances, may be so serious that it should almost always be determined directly, as by Penfield's method. In the determination of hygroscopic water, sources of error are: the fact that the air of an ordinary air bath is not dry, so that the powder cannot lose all its water, and the tendency to readsorption of moisture from the atmosphere by the powder, even in a closed desiccator. These, however, will seldom be serious in ordinary work.

In the determination of the other minor constituents the possible errors are of such slight absolute importance that special mention of them here is uncalled for. They will be spoken of when necessary in their respective places in the descriptive part, and should be guarded against in accurate work, of course. As Hillebrand remarks, however, in regard to the rarer elements, "it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent."

4. Time Needed for Analysis.

While the time necessary for most of the separate parts of the various analytical operations is conditioned by the circumstances of these in a more or less fixed way, yet the actual time in which the whole rock analysis can be finished depends—within limits—very largely upon the skill and judgment of the analyst. Thus, it will take a definite, minimum time to evaporate a given bulk of liquid, or to allow a precipitate, as that of ammonium magnesium phosphate, to stand. But an expert analyst will be able to complete many operations in much less time than can a novice. For example, the time needed for filtering and completely washing a precipitate can be reduced very materially with care and experience, and likewise the quantity of washing-water needed, which, in turn, will shorten the subsequent operations with the filtrate.

Again, while some of the operations are proceeding automatically the analyst can be carrying out others, and thus make use of time which would otherwise be wasted for the purposes of analysis. Or, the skilful chemist can carry out two filtrations simultaneously, while the attention of the novice will be fully occupied with one.

The analyst, therefore, should not be content to sit still and wait for each partial operation to be terminated before beginning another, but should avail himself of all the opportunities which present themselves for carrying on simultaneously as many separate operations as it is possible to do with success. The ability to do this naturally grows with experience in regard to the purely mechanical execution, and also with judgment as to the best way of economizing time. It is not to be recommended that the novice should attempt very much in this way, and he will probably find that one or two operations at once are all that he can cope with successfuly at the start. But he should constantly bear in mind the manifold possibilities in this direction, and, with growing experience, avail himself of the various opportunities that present themselves.

With some practice, the number of different operations, both active and passive, which may be conducted simultaneously or nearly so, may easily reach six or more. Thus, while filtering the first precipitate of ammonium-magnesium phosphate, the solution of alkali chlorides can be evaporating, the reduced iron solution be boiling down to expel H_2S, the precipitate of calcium oxalate ignited, ferrous oxide or water be determined, and the precipitates by which phosphoric anhydride, sulphur, baryta and zirconia are determined can be standing and filtered successively. Any such combination implies, of course, a sufficiently liberal supply of apparatus so as not to be kept waiting for lack of the necessary utensils, and it also implies the ability of the analyst to devote several hours continuously at a time to the analysis.

To come down to concrete figures,* it is easily possible to finish an analysis involving the determination of eighteen or twenty constituents in five days, not necessarily consecutive, of eight or ten hours each, and even in less time. Such an analysis can surely be made in six days without any special effort at economizing time. Indeed, a comparatively simple analysis, in which a dozen constituents are to be determined, may be completed readily in four, or even in three, days without any sacrifice of accuracy, but this last is possible only in the hands of a quick and experienced worker.

In the present section some suggestions are made of the possibilities in the way of shortening the time of analysis. They are not intended to be final, but will serve merely as guides in laying out the plan of analytical work, and are subject to modification to suit the exigencies of each particular case. In connection with them some estimates are given of the amount of time which is needed for the several operations and determinations. These, again, must be regarded as only rough approximations, which will vary with differing laboratory facilities and according to the skill and experience of the operator. They will have to be extended somewhat when conducted by a novice.

* Cf. Hillebrand, Bull. 176, p. 22; Bull. 305, p. 28.

Assuming that we start one morning at eight o'clock, with about 50 grams of rock chips, these can be reduced to powder ready for analysis in about an hour. The main fusion with alkali carbonates is then begun, the time needed for the fusion and cooling being about an hour. After this, the solution of the cake in hydrochloric acid and preparation for evaporation are carried out, which may be completed in half an hour or so, when the first evaporation is commenced. In the meanwhile, during the fusion with carbonate, the portion for phosphoric anhyride may be weighed out, digested with acid and evaporated, or some other minor determination started. This first evaporation for silica will be over by three o'clock, and during its continuance the precipitation of phosphoric anhydride by ammonium-molybdate and the fusion of the portion for total sulphur, zirconia and baryta, and some of the succeeding operations can be done. The filtration of the silica will take nearly an hour, after which the filtrate is placed on the water-bath and the second evaporation continued till dark, or overnight if possible and necessary, so as to be ready for filtration the next morning. Time will usually be found in the afternoon for the determination of hygroscopic water.

The second day begins with the second filtration of silica, and its washing, which will take in all an hour and a half or less. While the silica is being dried in the crucible and ignited, which lasts an hour or more, the precipitations of alumina, etc., may be made, three of which will consume nearly two hours, bringing us to lunch-time. During this the weighed silica may be evaporating with hydrofluoric acid, so as to be ready for the ignition and weighing of the crucible and residue after lunch. The filters and moist precipitate of alumina, etc., are next dried and ignited, for which nearly two hours are required. While this is going on, the filtrate can be precipitated twice with ammonium oxalate, and the ammonium-sodium phosphate added to the filtrate, to stand overnight for complete precipitation. After the ignition of the ammonia precipitate, its fusion with acid potassium sulphate can be begun and continued during the rest

of the afternoon, by the end of which it may generally be concluded. If not, it may be continued for an hour or so the next morning to completion, but the fusion should not be continued overnight. Ignition of the calcium oxalate and weighing of the lime may finish the day's work.

On the third day the determination of the alkalies is begun, the grinding, mixing and subsequent fusion taking up about two hours. While this fusion is in progress, the fusion of the ammonia precipitate with acid potassium sulphate being complete, the cold cake is dissolved in water, filtered for the trace of silica, the solution reduced with H_2S, and the excess of this boiled off, after which the solution is cooled and the total iron determined, all of which will take an hour or two. The intervals and the rest of the morning are occupied with the solution of the fusion for alkalies in water, and the precipitation of the filtrate with ammonium carbonate, or the decomposition of the rock for the manganese determination. During the first of the morning also half a liter of water may be boiled and allowed to cool, so as to be ready for the iron determinations. The evaporation of the filtrate containing the alkali chlorides may be begun before lunch, or immediately after it, and will usually last several hours. The solution from the total iron determination is evaporated on the water-bath if necessary in preparation for the titanium determination next day. As a supply of cold, boiled water is now available, the determination of ferrous iron may follow that of total iron, and will be completed in less than half an hour by the simple method given elsewhere. A duplicate determination may also be made if desired. During this afternoon the magnesia precipitate is dissolved and reprecipitated, and then filtered through the Gooch crucible, ignited and weighed. Finally, the dried alkali chlorides are freed from ammonium chloride by heating, brought into solution, filtered, and the evaporation in a weighed platinum crucible begun, which may be advantageously carried on overnight.

The fourth day is taken up with the determination of potas-

sium, titanium and combined water, the finishing off of the operations for phosphorus, manganese, barium, etc., if these have not been done before in appropriate intervals.

The above is an outline of my usual procedure, and it must be noted that a working day of nine or ten hours, with an hour's intermission for lunch, is postulated to allow some leisure, but with skill and application days of eight hours will suffice. It will be found that there are many enforced pauses in the course of the main operations, during which the various portions of the determinations of phosphorus, barium, chlorine and other minor constituents can be easily carried out. The volumes of liquid used for these are so small as a rule that the filtrations and other operations involved will each consume little time.

5*a*. Fusion with Alkali Carbonate.

A number of minerals, as leucite, nephelite and olivine, are easily and completely decomposed by hydrochloric acid, and their analysis may be effected after such a simple preliminary solution. Others again, as quartz, orthoclase, albite, pyroxene and hornblende, are either quite unattacked or only partially decomposed by this medium. Since practically no igneous rocks, so far as we know, are composed entirely of the first class of minerals and are completely soluble in hydrochloric acid, it is necessary to bring their constituents into soluble form by other means, as a preliminary to their analysis.

A number of methods have been proposed for this purpose, some of them based on the use of hydrochloric, sulphuric or hydrofluoric acids, and others involving the use of various fluxes, as alkali carbonates, calcium carbonate, lead or bismuth oxide and boric acid. A description and discussion of some of these is given by Hillebrand,* but it is unnecessary to enter into this phase of the matter here. It will suffice to describe only those methods which commend themselves to the author and to the chemists of the U. S. Geological Survey.

* Hillebrand Bull. 176, p. 47; Bull. 305, p. 68.

In order to determine the different constituents of a rock different methods of decomposition are found to be appropriate, depending on the constituents to be determined in a given portion. Those with which we shall have to deal are: fusion with alkali carbonate for the determination of all the main constituents except ferrous iron and alkalies, as well as for zirconia, baryta, etc.; fusion with calcium carbonate and ammonium chloride for the alkalies; solution in a mixture of sulphuric and hydrofluoric acids for ferrous iron and for manganese, nickel and copper, and simple digestion with hydrochloric or nitric acid for sulphuric anhydride and phosphoric anhydride and chlorine respectively.

The method of fusion with alkali carbonate depends upon the fact that this reagent at the temperature of fusion decomposes the minerals present, forming silicate, aluminate, titanate, phosphate and zirconate of sodium and potassium, and carbonates, silicates and possibly aluminates of iron, manganese, magnesium, calcium and barium, all of which are readily decomposed by and soluble in hydrochloric acid.

About 1 gram of rock powder is needed for this operation. A platinum crucible of 40 or 50 c.c. capacity is selected. A smaller one is less appropriate, on account of danger of loss through bubbling of the melted mass, as well as on account of greater difficulty in loosening the solid cake. For this fusion the sides of the crucible should have considerable flare, and one with vertical sides is unsuitable. It is cleaned, ignited to bright redness, placed in the desiccator after it has cooled below a red heat, and allowed to cool. When perfectly cold, it is weighed with the cover on, the weighing being carried to tenths of a milligram by means of the rider,* and the weight noted.

A gram is then added to the weights in the pan (usually the right-hand one), and the crucible placed on the weighing-table with the cover off, the forceps being used to handle it.

* It is to be understood that all weighings, except the rough ones of fluxes, are to be carried out to tenths of a milligram.

Some of the rock powder is poured into the crucible from the specimen tube and the covered crucible replaced on the balance-pan. If not enough powder has been poured in to balance the extra gram the operation is repeated, very small portions being added at a time from the specimen tube, till the weights in the right-hand pan are just about balanced. One very soon judges from the movements of the pointer whether the difference is large or not. If too much is added, small portions are removed from the crucible by a small platinum spatula or the handle of the forceps, and replaced in the specimen tube.* The correct weight is then carefully taken, also to tenths of a milligram, and the result noted in the line above that of the empty crucible as Cruc.+Subst. The difference will be the weight of substance taken.

An alternative method of weighing consists in weighing the uncorked specimen tube with the rock powder, pouring out carefully about a gram into the (unweighed) crucible, and then weighing the tube a second time. The loss in weight will be the weight of substance taken.† Of the two, the former is to be preferred here, as rather the more convenient, though either may be used.

In either case, care must be taken that no rock dust falls on the crucible cover, and in the second method that every particle of powder from the tube falls into the crucible. None of the rock powder should be allowed to fall on and adhere to the sides of the crucible, as this will not be acted on by the flux.

It is not necessary, indeed it is better not, to weigh out exactly 1 gram, which will take considerable time, but an amount varying from 0.9 to 1.1 gram should be taken, preferably a little more than a little less than a gram. With some practice it will be found simple to estimate with the eye when one has about the right amount.

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* In these operations the balance must be clamped and the crucible removed from the pan.

† This method is described in detail under the alkali determination.

The crucible (covered) and the weights being removed from the balance, one of a pair of balanced 3-inch watch-glasses is placed on the right-hand pan, and a 5-gram weight placed on it. On the other watch-glass a mixture of dry, powdered anhydrous sodium carbonate and potassium bicarbonate, or anhydrous sodium carbonate alone, is placed by means of a dry horn spoon, which is kept for this purpose in the balance-case drawer, and which must be carefully wiped off at the end of the operation. Enough is added or subtracted to balance the other watch-glass and the 5-gram weight. It is not necessary to weigh this accurately, but the difference should not be more than a few decigrams either way. It is usually stated that the amount of carbonate should be four times that of the substance taken, but it is found that a somewhat larger amount is advisable for proper fusion, and for very basic rocks as much as 6 grams may be taken advantageously, as with these the fusion is less perfect.

The crucible is placed on a clean sheet of paper, the cover laid to one side, and the greater part of the alkali carbonates transferred to the crucible by means of the platinum spatula, care being taken that none of the rock powder is thrown out. About half a gram of carbonate should be left on the watch-glass. The rock powder and the flux are carefully and thoroughly mixed in the crucible with the spatula, attention being paid to getting the carbonate well down at the bottom, and that no patches of rock powder are left at the angles or remain unmixed. After this thorough mixing, the surface is levelled down with the spatula, and this is well rubbed and cleaned off against the carbonate in the watch-glass, which is gently transferred to the crucible.

The covered platinum crucible is placed on a platinum triangle and heated over a low flame for about ten minutes, in order to decompose gently the acid potassium carbonate and drive off moisture. The heat is then increased till the mass sinters, so that the CO_2 may pass off without spattering, allowed to stay so for ten minutes or more, and finally brought

to complete fusion at a bright-red heat. The cover should be kept on during the operation, except when examining the contents, to catch any drops spattered from the molten mass, though none of these should be found on the under side of the cover if the operation has been done with care and the heat applied gradually.* As Hillebrand suggests, it is better to have the flame play obliquely against the bottom and lower sides of the crucible, and it is important that the flame does not envelop the whole crucible, to ensure an oxidizing atmosphere within it, and guard against any possible reduction by the gas. An occasional removal of the cover is advisable in order to effect this object, though not necessary.

The operation is at an end when the whole mass is in a state of quiet fusion, and no more bubbles are given off. The liquid will seldom be perfectly clear and transparent, as the carbonates of iron, magnesium and calcium will form cloudy masses within it, so that any such appearances need cause no concern. Indeed, with very basic rocks the mass may seem to be completely fused only around the edges, owing to the abundance of these infusible substances, although the rock is completely decomposed.

The crucible is taken from the flame and placed on a cool, flat surface of iron or polished stone. Such methods for quick cooling as using a blast of air, or dipping into water, are to be avoided, as they tend to injure the crucible and greatly shorten its life. Hillebrand recommends giving the crucible a quick, rotary motion before placing on the slab, so as to spread the melt over the sides in a thin sheet. This certainly has the advantage of rendering the subsequent disintegration in water more rapid, and also to some extent facilitates the separation of the cake from the crucible. It is not, however, necessary, and in general I am content to cool the crucible quickly but quietly on a slab of polished granite.

* If any such are found they should be fused by heating the cover upside down over the flame for a few minutes.

During the first moments of cooling the melt should be watched, and if it is seen to bubble or form miniature craters, it may be taken as evidence that the decomposition and expulsion of CO_2 is not complete. In this case the whole should be remelted and kept at a bright-red heat for another ten minutes.

When the crucible is finally cold, it is well to place it again over the full flame and heat it till the edges are melted, when it is to be removed and placed again on the slab till cold. This renders the removal of the cake from the crucible far easier, as a rule. A very important point to be borne in mind is that the crucible and its contents must be *thoroughly cold* before the process of removal is begun. The contents must be so cold that they separate either wholly or partially from the metal walls, which is often indicated by a ringing sound. If water is poured into the crucible before this happens the removal of the cake will probably be a difficult and lengthy proceeding. It is always better and time saved in the end to be patient during the cooling process and to allow the crucible to stand more time than may be actually needed, than to incur the possible annoyance of a cake that obstinately refuses to be extricated whole.

When a considerable amount of pyrite is present in the rock, it is necessary to oxidize the sulphur, to avoid attacking the crucible and the formation of an alloy between the iron and platinum. This may be done by adding a very little KNO_3 to the carbonates. But even a small quantity of this gives rise to effervescence, through reaction with the carbonates, and hence increases the possibility of loss through spattering. There is also danger of attacking the crucible through the action of the nitrate. It is therefore better in such cases, after weighing the rock powder and before the addition of the alkali carbonate, to roast the rock powder in the open crucible at a low red heat, insufficient to sinter, and far less to fuse, the rock. The mass can then be mixed with the carbonates and the fusion proceeded with, as described above.

As a general rule the cooled cake will be of a bluish-green color, due to the formation of sodium manganate. If no reducing

agents were present during fusion, and regularity in the formation of the color could be counted on, the depth of this color would serve as an excellent basis for estimating the amount of manganese. This might be made very precise by the preparation of standard cakes of sodium carbonate, fused with varying amounts of MnO, and preserved in glass tubes for reference. The possibility of the adoption of such a method, however, is seriously interfered with by the usual presence of ferrous oxide, which, by its reducing action, introduces serious irregularities in the depth of color. It often happens that rocks high in ferrous oxide, and containing considerable manganese, show in the cooled melt not a trace of the characteristic green, but only a muddy-brown color, due to the disseminated ferric carbonate.

Hillebrand also attributes certain irregularities to the occasional presence of a reducing atmosphere within the crucible, under conditions which are little understood. Thus it may happen that "two fusions made side by side or successively, under apparently similar conditions, may in one case show little or no manganese, in the other considerable." It is probable that all rock analysts have had similar experiences.

Before describing the removal of the cake from the crucible, one or two points in regard to the crucible itself may be touched on. From a new or little-used platinum crucible, with the ordinary amount of flare, the extraction of the cake usually offers no special difficulties, if attention be paid to the small points mentioned above and given below. But after a platinum crucible has been in use for some time, especially when often heated over the blast, the bottom tends to drop, and so alters the shape of the lower part. The smooth, single, interior concave curve becomes a double, ogee-like one, and, being slightly convex inwardly, frequently gives rise to difficulty in removing the cake When the crucible which is used for the carbonate fusion gets into this condition, it is well to return it to the maker and have it re-formed.

As all dents and other irregularities are apt to give rise to difficulty, the platinum crucible should never be allowed to fall

or become dented. Above all, any squeezing or other violent pressure should be avoided in attempting to loosen the melt, as any such deformations will greatly decrease the usefulness and value of the crucible. Caution on these points may seem superfluous, but one sees so often battered crucibles in use in laboratories, especially in the hands of students, that the reference to them may not be amiss.

The thoroughly cold crucible containing the cake is placed on a platinum triangle and nearly half filled with water. After standing for a minute, so as to allow the water to creep below the cake, it is gently heated over a small flame, that of an ordinary glass alcohol lamp being convenient, as it is not too intense. The flame is cautiously applied, especially around the edges of the cake, all boiling being avoided, as likely to lead to loss. After the edges are freed, the bottom is gently heated, when, under favorable circumstances, the cake loosens. This may be aided very materially by gently prying it up with a piece of thick platinum wire, one end of which has been hammered or filed to a wedge, and which serves as a miniature crowbar. This must be used with great caution, so as not to dent or pierce the sides of the crucible.

If this first operation is not successful, the fluid is carefully poured out into the platinum basin, any drops running over the edge being washed into the basin with a few drops of water from the wash-bottle. The crucible is then again half filled with water, and the operation repeated. Two or three repetitions will usually be sufficient to attain the object. When the cake is loosened it is transferred to the platinum basin, and the crucible washed slightly, so as to transfer any loose particles to the basin. Small fragments of the melt adhering to the sides of the crucible may be allowed to remain, and the crucible is covered and laid to one side for treatment later. The platinum basin containing the cake, and not more than one-third filled with water, is heated on the water-bath, or over a low flame, so as to avoid boiling, until the cake is easily broken up with the spatula, and it is finally dissolved as far as possible. This is indicated by the absence of

any hard portions of the cake. The presence of small, hard, black grains need not cause uneasiness, as magnetite and ilmenite are only attacked with difficulty by sodium carbonate, and these will be dissolved later, but it is highly advantageous that the melted mass be completely dissolved.

If the cake should prove obstinate and refuse to loosen from the crucible, one of two plans may be followed. The one preferred is to dissolve the cake in the crucible itself over a low flame or on the water-bath. The liquid in the platinum basin may be used for this, in small portions at a time, the crucible being emptied back into this each time. The other consists in placing the crucible on its side in the basin, filling this with water about one-third full, and heating gently till the cake is dissolved. The crucible is then lifted out of the basin by means of a stirring-rod, and thoroughly washed, inside and out, the washings falling, of course, into the basin.

If the cake is colored a deep green, on the addition of hydrochloric acid chlorine will be evolved, through reaction with the manganate, and will attack the platinum. To avoid this a few drops of alcohol are to be added to destroy the manganate.

When the cake is quite dissolved, the platinum spatula is removed and washed with a little water, and laid aside in a clean place. The basin is removed from the flame and covered with a watch-glass, which should project about an inch on all sides. This is, of course, placed with the convex side down, as must always be done with covering watch-glasses. Ten or fifteen c.c. of concentrated hydrochloric acid are measured off in a 25-c.c. measuring-cylinder with lip, and poured very gradually into the basin through a small funnel, the end of which has been somewhat drawn out and bent at an angle of 45°, so as to project into the basin through the lip-opening. This addition of acid should be very gradual, by a few drops at a time at first, so as to allow the effervescence to be as gentle as possible. It is also well to let the acid flow down the side of the basin below the lip, so that the drops thrown up by the

first, somewhat violent, effervescence may be directed away from the lip-opening. A pink blush, due to $MnCl_2$, indicates the presence of considerable manganese.

When all the acid has been added except 1 or 2 c.c. the tip of the funnel is washed into the crucible with a little water, and the funnel withdrawn. A few drops of acid are poured on the under side of the crucible cover, to dissolve any drops spattered from the fusion, and washed into the crucible with a very little water. The rest of the acid is then poured into the crucible, to dissolve any adhering portions of the carbonate, and slightly warmed, the crucible being kept well covered.

When all effervescence has ceased in the basin, the drops on the watch-glass cover are rinsed down into it, the glass being held vertically, with the part which has been next the lip downward and near the surface of the liquid in the basin. The rinsing is to be repeated several times, the stream being so directed as to let the water flow over all the wetted surface from top to bottom. The watch-glass is laid aside, and the sides of the basin above the liquid are washed down by a gentle stream from the wash-bottle, the basin being slowly revolved to facilitate the operation. One complete washing down all around will be sufficient. The contents of the crucible are then added, and this and the cover rinsed several times into the basin. When complete, if care has been used to avoid an inordinate amount of wash-water, the basin should be little more than half full.

As a little silica or silicate adheres persistently to the crucible sides, it is well to rub the inside of this with a small piece of filter paper, which is then thrown into the basin. This is later decomposed by the acid during the evaporation.

The platinum spatula is then put in the basin, and this placed on the water-bath for evaporation. The fluid should be clear, and contain no solid except some light, floating flakes of silica. There may be a few small black particles of magnetite or ilmenite present, which will dissolve in the hot acid. But if many small, hard, gritty particles are felt at the bottom,

it is evidence that the fusion has not been successfully carried out to complete decomposition of the rock, and the contents of the basin should be rejected, another portion of rock powder weighed out, and the whole operation of fusion with alkali carbonate gone through with as before.

5*b*. Silica.

Separation of Silica.—The fluid in the basin now contains all the rock constituents in solution as chlorides, except the silica, which is for the most part in solution as a soluble silicic acid, and partly as insoluble flakes. Our first object then is to separate the silica from the other constituents, so that it may be weighed. This is effected by evaporation to dryness, whereby the silica is rendered insoluble in water.

Hillebrand* has shown that a single evaporation will not attain this end perfectly, even with a subsequent heating at 110° to 120°, which is the method usually employed, but that a small amount of silica will go into solution and will not be wholly recovered in the later processes. He therefore recommends a double evaporation as conducive to the most accurate results, and his suggestion is followed here.

The first evaporation is continued, on the water-bath, until no more fumes of HCl are given off and the mass appears quite dry, the dark-yellow color of the moist salts changing to a pale-brown shade. During the last stages it is well every now and then to break up the gelatinous mass with the platinum spatula, which is kept in the basin, so that the water and hydrochloric acid may pass off more readily. When the mass becomes crystalline, the lumps may likewise be broken up, but this should be done with caution to avoid loss by flying off of particles of the salts, and is not necessary.

It is not necessary to heat the dried salts at a temperature of 110° or 120°, as is usually done. Indeed this is distinctly

* Hillebrand, Bull. 176, p. 52; Bull. 305, p. 75.

disadvantageous, since silicates (especially of magnesium) are liable to be formed, which dissolve in the hydrochloric acid added later, and thus lead to loss of silica. At the same time the heating at such a temperature will probably add considerably to the impurities in the silica (Hillebrand).

As soon as the mass is quite dry and free from all odor of hydrochloric acid, the basin is removed from the water-bath and the contents moistened to a paste with concentrated hydrochloric acid, to dissolve the basic salts and magnesia which are invariably formed during the evaporation. The small amount of salts adhering to the spatula must not be neglected. It is important here not to use a large quantity of acid, as this will tend to prolong the filtration, probably through reaction of the strong acid on the paper and consequent swelling and clogging of the pores. About 5 c.c. will be ample to moisten the whole thoroughly. The pasty mass should be thoroughly mixed with the spatula, some of it being rubbed around the line marking the original border of the liquid, where a band of somewhat strongly adherent silica is apt to form.

After standing and warming for a few minutes, the whole is diluted with water from the wash-bottle, the stream washing down the sides of the basin. The spatula should be well rinsed off and laid aside, leaning its broad end against the granite slab, as a little silica, (only visible when the spatula is dry), adheres to it persistently. A glass stirring-rod, about 2 inches longer than the diameter of the basin, is placed in this, which should be about one-third full of liquid. The basin with its contents is next heated on the water-bath or over a low flame, with occasional stirring, until the chlorides are entirely dissolved and only insoluble silica remains, as is indicated by the absence of gritty particles under the rod.

While the solution of the chlorides is being effected at a gentle heat, the filter may be made ready for the silica. A dry, clean 2½-inch (6.5 cm.) funnel is selected, preferably one with a suction-tube fused on (p. 35). A suction-tube may be connected by a short length of rubber tubing, but there is great lia-

bility to loss of liquid in the crevice between the glass and rubber, unless care is taken to wash this out later. A 9-cm. filter-paper is folded in the usual way, first along a diameter and then into a quadrant, opened out and placed in the funnel. If the apical angle of the funnel is 60° it will fit snugly. If not, the filter must be refolded the second time, not quite evenly, so as to form a trifle more than a quadrant, and opened out either on the larger or the smaller half, according as the filter was found before to be too narrow or too broad.

The paper is then moistened with water and pressed snugly home, air-bubbles being squeezed out gently with the finger, and the lines on either side made by the folds being well pressed down, especially at the rim, as they are liable to form air-channels and thus retard filtration, as well as possibly cause loss of silica if the filter happens to be filled above the rim. The funnel is then placed in a funnel-stand, and beneath it a 400-c.c. lipped beaker. The end of the suction tube should reach to within an inch or two of the bottom to avoid loss by splashing, and preferably near one side of the beaker. It should never dip into the filtrate, the funnel being raised from time to time to prevent this.

When the salts are entirely dissolved, the heated liquid in the basin is passed through the filter. The stream is directed by the stirring-rod held against the lip to the side of the filter, not the bottom, which is liable to break. The filter should not be allowed to fill more than to within 2 or 3 mm. of the edge, and must never be allowed to overflow, or particles of precipitate may be carried between it and the funnel, and there will also be a tendency of the liquid to creep up the glass sides. At first the clear, supernatant liquid is poured into the filter, which should not be allowed to quite empty. Finally the silica itself is poured in with the liquid, as washing by decantation is not necessary here.

It is highly important in all filtering operations to keep the tube part of the funnel, or the suction-tube, if there be one attached, full of liquid, so as to take advantage of the increased

suction due to the colum of liquid. This may usually be accomplished by care and attention to several points, the chief of which are: to moisten the interior of the tube of the funnel before fitting the filter (the suction-tube will not need this); to see that the filter fits tight to the funnel, and especially that there is no passage for the air along the lines of folds at either side;* to keep the filter from emptying, once the suction has been established, till all of the liquid has been filtered off. and the washing is to begin.

The ease with which this may be accomplished depends on the liquid, the funnel and the filter, all of which vary in this respect, but with practice the correct filling of the tube can be accomplished in nearly all cases with great readiness, and will very greatly reduce the time needed for filtering.

When all the liquid and silica that will flow readily have been brought on the filter, the basin is gently rinsed with a little cold water from the wash-bottle, the silica adhering to the sides being washed down to the bottom, and the liquid and as much of the silica as possible poured into the filter as before. When the filter is empty, the basin is held in the left hand, above the filter, with the stirring-rod across it and resting on the lip, the end of the rod an inch or so beyond, and the rod kept in place by the tip of the left forefinger. A gentle stream of water is then directed against the upper part of the basin, so as to wash the silica into the filter, and at the same time rinse the basin. When the filter is nearly full the liquid is allowed to empty and the operation repeated two or three times. It is not necessary here to wash thoroughly, or to bring all the silica into the filter at this stage, though this should be done as far as possible without too many rinsings.

In regard to the washing of silica it is of very great importance to note that only cold water should be used, as hot solutions of iron, unless strongly acid, have a tendency to throw down basic

* If bubbles begin to pass along these, the open ends should be gently pressed down and closed with the tip of the stirring-rod, and without breaking the paper.

salts, which will contaminate the silica. It sometimes happens that the silica in the filter is colored a brick-red through this cause, when hot water has been used for washing.

When the liquid has about ceased dropping from the last washing, the platinum basin is substituted for the beaker beneath the funnel- or suction-tube, taking care to lose no drops from the latter during the change. The contents of the beaker are poured into the basin, and the beaker itself rinsed once or twice, the rinsings going also into the basin. They are then interchanged once more, and the stirring-rod is placed in the beaker set beneath the funnel. The basin, with the platinum spatula in it, is once more placed on the water-bath for the second evaporation. It is better to cover the funnel with a watch-glass, and the beaker as well, for which purpose a perforated watch-glass (p. 34) is very convenient, as it allows the suction-tube to remain in place inside the beaker.

When the second evaporation is complete and the salts are reduced to dryness and free from HCl, occasional stirring with the spatula hastening the process, the mass is again moistened with a little (3 to 5 c.c.) hydrochloric acid, and, after standing a short time, about 50 c.c. of water are added, and the whole gently heated to complete solution (except for particles of silica).

This liquid is then filtered through the filter which holds the bulk of the silica, the funnel not being allowed to empty till all is through. The basin is rinsed as before, and all particles of silica washed into the filter by small jets of water. If any adhere, and indeed in any case, the interior of the basin should be gently rubbed all over with a rubber-tipped stirring-rod so as to free any strongly adhering particles, the zone of the upper border of the original liquid being especially attended to. The rubber tip should be slightly washed afterward by a jet of water. Cold water must be used throughout the washing process.

In washing, the filter must be allowed to empty before the addition of another portion of wash-water, so as to leave as little as possible of the soluble salts in the precipitate or funnel. This is highly important for facilitating the washing and reduc-

ing the bulk of water needed. Given the same bulk of washing liquid the removal of the soluble salts will be more complete if a number of additions of small volume are used rather than a few of large volume.*

When the basin has been rinsed out several times and all the silica is in the filter, the contents of this must be well washed. This is best done by stirring up the silica with the first few portions of wash-water, and afterward washing down the sides of the filter, so as to bring all the silica toward the bottom. Here the suggestion as to the addition of only small quantities of water at a time, and allowing the filter to empty after each, should be followed, so as to keep down the bulk of liquid.

This washing is to be carried out till a few drops from the end of the funnel give no chlorine reaction with solution of silver nitrate in a small watch-glass. In making this test, and in all similar cases, the end of the funnel or suction-tube should be washed off with a small jet of water, before collecting the drops for testing, as some of the fluid which has previously passed may have crept up the side, and by mingling with the drop may give a chlorine reaction, when the last portions of the liquid are, in reality, quite free from chlorides.

When washing is complete the bulk of liquid, including all the washings, in the 400-c.c. beaker will be from 150 to 200 c.c., which ought to be sufficient for complete washing if the operation has been conducted with care and due avoidance of excessive use of liquid.

Ignition of Silica.—A platinum crucible of 30- or 40-c.c. capacity is selected, preferably the latter if the rock contains much alumina or iron, ignited, cooled in the desiccator and weighed. The free edges of the filter in the funnel containing the silica are then folded down upon the silica, so as to completely enclose it, the platinum spatula being used for this purpose. The little package is then removed from the funnel and placed in the crucible by means of the spatula, preferably with the side

* Cf. Ostwald, pp. 18 to 21; Treadwell, p. 16.

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uppermost which has three thicknesses of paper. It is gently pressed down toward the bottom of the crucible, but the paper should not be torn, nor should all egress for steam from below be shut off. With a small piece of filter any particles of silica adhering to the spatula are rubbed off, and also any which may be on the funnel above the edge of the filter, and the piece of paper is also placed in the crucible.

In this way the silica can be dried in the crucible and ignited, with no danger of loss from whirling up of the light powder. This is preferable to the method recommended by Fresenius * of drying the filter and silica prior to ignition. In this latter method the danger of loss by handling the filter when the powder is dry is far greater. Incineration of the filter will be equally complete in either case.

The covered crucible is then heated at some distance above a low flame, to avoid boiling of the pasty mass, and probable loss of substance or spattering of it on the sides of the crucible. This is continued till the contents are dry and the filter begins to char. As the water is driven off the crucible may be gradually lowered, but this must be done with great caution, and the flame kept small. Also a filter which is carbonized at a low temperature is more easily incinerated than one which is carbonized rapidly and at a high temperature. The crucible is finally brought close to the flame and heated till no more smoke is given off. The escaping vapors should never be allowed to ignite, and consequently the flame should be kept low and the bottom of the crucible not brought to a red heat till carbonization is complete.

The full, or almost full, flame is then turned on and the crucible heated to a bright-red heat, being kept vertical and with the cover very slightly moved to one side, so as to allow the entrance of some air, but not enough to give rise to dangerous draughts. The flame, of course, should not be allowed to envelop the crucible, as an oxidizing atmosphere within it is

* Fresenius, I, p. 510.

essential. When the carbon is entirely consumed,* or almost so, the cover is put in place, a blast substituted for the Bunsen burner, and the crucible blasted for at least twenty minutes. This is necessary in order to effect complete dehydration of the silica, the last portions of water being retained with great obstinacy. It also has the advantage of rendering the silica non-hygroscopic (Hillebrand). If the blast is not available, the crucible must be heated several times to constant weight at the highest heat of the Bunsen burner. But in this case the expulsion of water is probably never quite complete, and the results for silica will therefore be a trifle high. The time needed for ignition will also be much longer. The cover should be examined to see if it carries any adhering carbon, and if so this is to be burnt off by heating in the flame.

The crucible and its contents are then cooled in the desiccator and weighed, reheating to constant weight not being necessary when the blast has been used. The result is to be recorded as Cruc. $+ SiO_2 + x$, above the weight of the empty crucible, and also in a place to the right of it.

The silica as thus obtained is never pure, but contains small amounts of Fe_2O_3, TiO_2, P_2O_5, and possibly other substances, and in basic rocks these may amount to several per cent. After weighing, therefore, the crucible is placed on a sheet of paper and the silica mixed with 5 c.c. of water. In doing this the tip of the wash-bottle should be filled with water by blowing before inserting in the crucible, to avoid blowing out any of the light silica by the first puff of air from the empty tip. Three or four drops of dilute sulphuric acid are then added, the presence of this being necessary to retain the TiO_2, some of which would be vaporized as titanium fluoride in the absence of sulphuric acid. Hydrofluoric acid is then poured in, a few drops at a time. The action is apt to be violent, but with care and sufficient moistening of the silica no loss need be incurred. The hydrofluoric acid should

* If the carbon of a filter-paper burns with difficulty, it will be well to remove the flame and allow the air to penetrate the cold carbon. On reheating combustion will usually be rapid.

be added in sufficient quantity to dissolve the silica on warming, not more than one-quarter of the depth of the crucible being ample for this purpose.

The crucible is then placed on the triangle of a special air-bath, such as is described and figured by Hillebrand.* If this is not available, a capacious porcelain crucible with an appropriate triangle made of iron or platinum wire will answer the purpose. The use of such an air-bath ensures uniform heating of the liquid at a high temperature, and hence prevents loss by boiling or spattering. The air-bath and the crucible within it are heated over a moderately low flame till the contents of the crucible are dry. This operation must be carried out under the hood, with a good draught.

The crucible is then ignited at a bright-red heat, blasting for a few minutes being advisable to ensure the decomposition of the sulphates of iron and titanium, and the complete expulsion of all traces of sulphuric acid. After cooling in the desiccator the crucible is weighed, and its weight noted as Cruc.$+x$ below that of Cruc.$+SiO_2+x$. The difference between the two will be the weight of silica, to which it is necessary to add later the weight of the very small amount of this which is recovered from the filtrate (cf. p. 109).

As pointed out by Hillebrand, the composition of this residue is variable. It always contains alumina, and ferric, titanic and phosphoric oxides, but very exceptionally baryta, and no lime or magnesia if the rock has been properly decomposed. The assumption that all the titanium is present is this, or that the residue consists almost solely of TiO_2, is quite unwarranted.

The crucible containing the impurities in the silica is laid aside in a desiccator or other safe place, *uncleaned*, for use in the subsequent ignition of the precipitate of alumina, etc. (p. 104).

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* Hillebrand, Bull. 176, p. 23; Bull. 305, p. 29.

5c. Alumina and Total Iron Oxides.

In the filtrate from the silica, the alumina, iron oxides, titanium, zirconium, and phosphorus oxides are best separated from nickel, lime, magnesia, and the alkalies, by precipitation by ammonia water, in the presence of sufficient ammonium salts to prevent the coprecipitation of magnesia. This method is the simplest, is very reliable, consumes very little time, and permits of the complete separation of manganese at this point, so that it is the one recommended for general use. A description of the sodium acetate method will, however, be given, in case its use be deemed desirable, but in general and especially in the hands of the novice it should be avoided. The advantages and disadvantages of the method have been discussed previously.

Precipitation by Ammonia.—To the filtrate from the silica in the 400-c.c. beaker, which should amount to from 150 to 200 c.c. in bulk, about 10 c.c. of concentrated hydrochloric acid are added.* The object of this is to form ammonium chloride on the addition of ammonia, in sufficient quantity to prevent the precipitation of magnesia along with the alumina and iron. One should also avoid a large excess of ammonium chloride, so that for rocks like granites and trachytes, which contain but little magnesia, the addition of about 5 c.c. of HCl will be sufficient. If the rock is basic and extremely rich in magnesia, 15 c.c. will probably not be too much.

At this point the analyst has to decide whether or not to precipitate the manganese with the alumina. For accurate work my preference is for the coprecipitation, especially if the rock is rather low in silica and the color of the carbonate melt showed that considerable manganese is present, because it thus affects the alumina alone and can be corrected for by a separate determination. In this case about one gram of solid ammonium persulphate, which has been specially purified, is

*The addition of nitric acid is not necessary, as the ferrous iron will have been changed to ferric during the fusion and the two evaporations.

added to the liquid in the beaker. The manganese will be thrown down as peroxide, but nickel and chromium will remain in solution, the former as an ammonium double salt, and the latter as chromate. Cobalt will be precipitated, but as only traces of this are ever present, this is of no moment. Hillebrand* points out that if the rock carries appreciable quantities of barium or strontium, or is very rich in lime, the use of the persulphate in not advisable. But two, and certainly three, precipitations will surely get all the lime into the filtrate in any igneous rocks, any barium which may come down can be collected and allowed for later, and it is only in very exceptional cases that the amount of strontium is appreciable here. If the rock is high in silica or is low in manganese (less than 0.20 per cent), the analyst may advantageously dispense with the addition of the persulphate, and disregard the slight error involved in the distribution of the manganese among the alumina, lime, and magnesia.

After the addition of the hydrochloric acid and possibly persulphate, the liquid is heated almost to boiling, and ammonia water † is added gradually and with constant stirring till the liquid smells rather strongly of ammonia.‡ The beaker is then heated to boiling, and kept boiling for not more than a minute. As has been pointed out by several chemists, it is quite unnecessary to boil off the excess of ammonia, as is usually recommended (Fresenius), and indeed this might lead to re-solution of some alumina through decomposition of the ammonium chloride and formation of hydrochloric acid (Fresenius, Classen).

The bulky gelatinous precipitate is allowed to settle for only a few minutes, and then filtered through an 11-cm. filter placed in a 3-inch (7.5 cm.) funnel, provided with a suction-tube fused

* Hillebrand, Bull. 305, p. 85.

† If this is not fresh, it should have been previously tested with $CaCl_2$ to see if ammonium carbonate is present.

‡ If the ammonia water has been poured down the side of the beaker, this should be rinsed down with a little water, as a strong odor of ammonia might otherwise be noted, although the fluid is still acid.

to its lower end. The filtrate is caught in an 800-c.c. beaker. The clear liquid* should be at first decanted as far as possible from the precipitate, though several washings by decantation, as usually recommended, are quite unnecessary and add much to the bulk of the filtrate. The precipitate is then brought on the filter, care being taken that the filter is neither filled to more than 2 or 3 mm. of the edge, not that it runs dry, as the latter will tend to consolidate the gelatinous hydroxides and render the filtration and washing long and tedious.

The beaker is rinsed out two or three times with hot water, each addition being passed separately through the filter, and any loose particles of precipitate also being washed into it, though complete cleaning of the beaker is not necessary.

The tendency of such gelatinous precipitates as those of aluminum and iron hydroxides to run through the filter has often been remarked. This may be due in part to partial solution in hydrochloric acid formed by decomposition of ammonium chloride if the excess of ammonia is expelled by boiling, as explained above; and partly to the property (noted by Ostwald) in such colloidal bodies of indeterminate solubility in water. This can be prevented by the presence of crystalline salts in the solution, which precipitate such pseudo-solutions.† As also pointed out by Ostwald, a high temperature is favorable to the precipitation of such colloidal solutions, and this will explain, at least in part, the tendency of the precipitate to pass through the filter as the filtration proceeds and the liquid becomes cool.

To rectify this Penfield and Harper‡ recommend the use of a dilute solution of ammonium nitrate for washing, obtained by neutralizing a solution of 2 c.c. of concentrated nitric acid in 100 c.c. of water by ammonia. For the most exacting work, and especially for almost purely aluminous precipitates, this may be used, as these two chemists made their observations on pure solutions of aluminum chloride. In the case of rocks, however, with

* A greenish tinge rarely observed in this filtrate is due to nickel (see p. 126).

† Cf. Ostwald, p. 24.

‡ Penfield and Harper, Am. Jour. Sci., XXXII, p. 112, 1886.

their more complex ammonia precipitates, I have been seldom if ever troubled in this way, and, as the first precipitate is not washed thoroughly to complete freedom from salts, pure, hot water alone may be used for the washing without danger.

After rinsing the beaker, then, the precipitate in the filter is washed several times with hot water, the stream from the wash-bottle breaking it up more or less. In this operation great care should be taken not to throw too hard or sudden a jet onto the precipitate, which might easily throw some of it out of the funnel. Complete washing is not necessary at this stage, but the precipitate should be collected in the bottom of the filter, and the upper edges washed clean.

As it is invariably to be assumed that this first precipitate contains magnesia as well as some lime and alkalies, its solution and reprecipitation at least once are necessary in all cases.

With the platinum spatula a side of the filter is loosened and a channel made between the filter and funnel to the point, so that all the liquid in the suction-tube and tubular part of the funnel may run out into the beaker below. The uncleaned stirring-rod remains in the 400-c.c. beaker and this is placed conveniently near the edge of the table. The funnel is removed from the stand, and the filter gently loosened all around with the platinum spatula, the edges being turned down as little as possible, and the paper not being torn. The funnel is then held with its side horizontal and the folded part of the filter underneath, the spatula slipped beneath this, and the filter with its contents gently removed from the funnel, carefully dropped into the 400-c.c. beaker, and the funnel is replaced in its stand. If any of the gelatinous precipitate has soiled the funnel above the filter, it is to be wiped off with a small piece of filter paper, and this is also placed in the beaker.

About 100 c.c. of water is then added, and concentrated nitric acid in some excess, about 10 c.c. being ample in most cases. The liquid is then heated gently until all the precipitate is dissolved. The filter paper is broken up and shredded with the stirring-rod, until it is wholly macerated and disintegrated

into small pieces and fibers. The object of this maceration, which is due to Dittrich, is to distribute the fibers of cellulose throughout the gelatinous hydroxide precipitate, so that the oxides will be left, on ignition, in a fine state of division, and not in the usual lump form, thus permitting the ready reoxidation of any reduced ferric oxide, and also greatly facilitating the subsequent solution in pyrosulphate.

The solution is then precipitated with diluted * ammonia water in slight excess, the filter being also moistened with it, and, after stirring, the whole is brought to a boil. In the meantime another 11-cm. filter has been fitted to the same funnel as before, the 800-c.c. beaker being in place below it. In fitting the filter no more water than is needed to moisten the paper should be used, to avoid undue bulk of liquid. The contents of the 400-c.c beaker are filtered through this as before, and the filter and its contents are washed with hot water, as well as the 400-c.c. beaker.

If the rock is basic and contains much magnesia or lime, as the diorites, gabbros, basalts, tephrites, and peridotites, a second solution in nitric acid and reprecipitation is to be made, this being carried out exactly as before, including the maceration of the filter. In this case the washing of the second precipitate need not be thorough. It may occasionally happen that a third reprecipitation is called for, if the rock is exceptionally high in magnesia, or in lime if the persulphate has been used, but this will seldom be necessary.

The use of nitric acid instead of hydrochloric for the solution of the precipitate is recommended by Penfield and Harper. This should always be used, as it very greatly facilitates the final washing by reducing the amount of HCl present, and so makes the final bulk of filtrate much less. It is essential that the precipitate be washed free from all traces of chlorine, as aluminum and ferric chlorides are volatile and the presence

* If concentrated ammonia water is used the action with the heated acid is so violent that there is danger of loss.

of chlorides will lead to their formation and loss on ignition.*

After the final precipitation, whether it be the second or third, as much of the precipitate as is easily possible is to be got directly on the filter in the funnel. The sides of the beaker are washed down with strong jets of hot water, so as to loosen the adhering precipitate, and this and the washings poured into the filter. To remove the last remaining portions of precipitate, which adhere tenaciously to the sides, small pieces of filter paper (half a 7-cm. filter will serve), are used as swabs, and rubbed with the end of the stirring-rod all over the sides of the beaker, the rod itself being cleaned with another piece, and all these papers passed into the filter in the funnel above the main mass. Three or four such rubbings with paper will usually serve to render the interior of the beaker perfectly clean. The contents of the filter are washed with many small portions of hot water, the mass being broken up and collected in the bottom of the filter, and the edges cleaned till no chlorine reaction is to be obtained from the last drops. For ordinary work, in the case of a third precipitation, only the rinsings and first washings need be caught in the beaker, as the amount of magnesia or lime in the final ones would be inappreciable, and they would add considerably to the bulk of liquid. The contents of the beaker are to be kept (covered) for the determination of lime and magnesia.

The funnel containing the precipitate is then laid aside, well covered with a large round filter folded down all round the edges. If the amount of iron be great, as may be known by the mineral composition of the rock, or by the depth of color of the precipitate, and if macerated filter paper is not mixed with the precipitate, the filter (in the funnel) may be placed in an air-bath and heated at a temperature of 110° till the precipitate is thoroughly dry. In general it will not be

* Hillebrand (Bull. 305, p. 83, note) states that aluminum chloride is not vaporizable under the conditions of ignition.

necessary, and the precipitate may be ignited from the moist condition as described below.

Precipitation by Sodium Acetate.—To the cold filtrate from the silica, which contains a little free acid, and whose volume is about 200 c.c., a concentrated solution of sodium carbonate is added cautiously till the fluid turns a dark red and a slight turbidity is observed, which does not disappear on stirring. This addition may be made in the beaker covered with a watch-glass, and the solution of carbonate introduced through the small funnel with bent tip, so as to avoid loss by effervescence. The watch-glass, tip of the funnel, and the sides of the beaker should be rinsed down, and if these rinsings are sufficiently acid to redissolve the slight precipitate, as may sometimes happen, a few more drops of carbonate solution are to be added till a slight permanent precipitate is formed again.

Dilute hydrochloric acid is then to be added, drop by drop and very cautiously, with constant stirring, till the slight precipitate and turbidity *just* disappear, but the fluid still retains its deep-red color. Especial caution is needed here, as any decided excess will set free enough extra acetic acid from the sodium acetate added subsequently to render the precipitation of alumina and iron incomplete. If too much has been added, therefore, the solution is once more to be slightly more than neutralized with sodium carbonate and again treated with dilute hydrochloric acid more cautiously.

Enough acetic acid of specific gravity 1.044 (33 per cent) is poured in to form about 3 per cent by volume of the total liquid, preferably rather less than more. As the final volume will be about 300 c.c., 8 or at most 10 c.c. of acetic acid are sufficient. If too little is present a slight precipitation of manganese is to be feared, while if too much free acid is present alumina and iron will not be completely thrown down, but will pass in small amount into the filtrate.

About 2 grams of sodium acetate dissolved in a little water are then added. This is the amount for the generality of rocks,

but it may be varied somewhat with advantage. Thus for rocks low in the sesquioxides, as granites and rhyolites, 1½ grams may serve, though 2 will not be amiss. But in such rocks as foyaites, phonolites, gabbros, basalts, or tephrites, which contain large amounts of these oxides, the quantity had best be increased to 3 grams, which may be considered the limit.

If the liquid has not a volume of 300 c.c., it is diluted to this bulk, or to 350 c.c. if the larger amount of sodium acetate has been used. It is heated to boiling and allowed to boil for not more than a minute or two, as prolonged boiling renders the precipitate slimy and difficult to filter. After settling for a few minutes, the liquid is filtered through an 11-cm. filter, and washed only two or three times with hot water. This precipitate, which consists of basic acetates of aluminum and iron, with the titanium, zirconium, chromium and phosphorus of the rock, is rather more apt to run through the filter than the precipitate of hydroxides produced by ammonia. The washing, therefore, should not be thorough, and it is as well to add a little sodium acetate to the hot washing-water, so as to have a crystalline salt present.

After this slight washing the precipitate is dissolved in nitric acid by the method described on p. 100, reprecipitated with ammonia water, and this solution and reprecipitation repeated if the rock is basic, exactly as was done in the method by ammonia alone. The final precipitate is to be ignited as described below. It must be remembered, however, that there will be undoubtedly another filter containing the alumina and iron which have passed through with the filtrate, so that the ignition of the main portion must wait till this has been incinerated with the extra filters, to avoid reduction of the ferric oxide. Otherwise ignition in a separate crucible and consequently two fusions with potassium pyrosulphate are involved. For the treatment of the filtrate, see pages 124 and 126.

Ignition of the Precipitate.—Assuming that the precipitate has not been dried, as is generally the case, the 11-cm. filter

containing it is placed moist in the crucible which has been used for the determination of silica, and in which there still remain the impurities left on evaporation with hydrofluoric acid. This is done with the aid of the platinum spatula, the free edges of the filter being folded over inwards, the mass very gently freed from the funnel without tearing the paper, and the whole carefully placed in the crucible with the three-fold portion uppermost. Care should be taken not to soil the sides of the crucible, and to leave abundant free passage for the exit of steam from beneath the mass. The spatula and the interior of the funnel are to be cleaned with a small piece of filter paper, which is laid on top of the package in the crucible.

The drying of the moist mass must be done very cautiously, at a considerable height (8 inches or so) above a small flame, the crucible being vertical and covered. Constant watching is necessary at first to prevent any bubbling of the pasty mass, which would soil the upper sides of the crucible with precipitate and render its complete solution in fused $KHSO_4$ difficult. The crucible is very gently and cautiously lowered as the mass dries off, until the filter is carbonized, when it is heated vertically for a short time at a bright-red heat till the cover is free from adhering carbon.

The crucible is then laid on its side on the platinum triangle, the mouth at one of the angles, and the cover is leant against it, at a small angle, with its upper edge a little below the top of the crucible, leaving a narrow opening above and below. As the cover is apt to slip down, it is well to make several small grooves with a file at the angles of the triangle used for this operation, so as to hold the cover in place. The flame is directed against the bottom and lower third of the crucible, the flame not being violent enough to cause dangerous draughts, and the incineration of the paper is quickly accomplished. It is then heated at a bright-red heat for at least twenty minutes. This will ensure complete incineration of the filter and, to a very large extent, the reoxidation of the ferrous oxide which may be formed in small quantity. As the last portions of water

are not always driven off by the heat of a Bunsen burner, it is best to blast for five or ten minutes in order to effect the complete dehydration of the alumina.

If the amount of iron is considerable, and macerated paper has not been present in the precipitation, the precipitate should be dried in an air-bath as described above. The filter is freed from adhering precipitate as far as possible, by reversing the dry filter over a small sheet of glazed, white paper, and gently crinkling and pressing the paper cone till the precipitate is loosened and falls on the paper. The filter, almost free from precipitate, is placed in the crucible, carbonized and incinerated as before, after which the precipitate is placed in the crucible and ignited as below. The object of this procedure is to avoid as far as possible the reducing action of the paper and carbon on the ferric oxide, it being almost impossible to thoroughly reoxidize the ferrous oxide so formed by any reasonable ignition, even after moistening with nitric acid (Penfield, Hillebrand), if the ignited precipitate is lumpy.

After cooling in the desiccator the crucible is weighed, and the difference between this and the weight of the empty crucible, obtained prior to the ignition of the silica (p. 93), is that of the Al_2O_3, total iron as Fe_2O_3, Mn_3O_4, TiO_2, ZrO_2, P_2O_5 and a trace of SiO_2. This may be noted as $Al_2O_3+Fe_2O_3+x$. The amounts of these various constituents are determined separately, and that of the alumina arrived at by difference.

The ignited precipitate in the crucible is used for the determination of total iron, titanium dioxide and the trace of silica, its solution being effected by fusion with potassium pyrosulphate. This process may be advantageously begun immediately after weighing, as it takes several hours.

Fusion with Potassium Pyrosulphate.*—The ignited precipitate of alumina, ferric oxide, etc., is used for the determination of both total iron and titanium. It may be brought

* Hillebrand (Bull. 305, p. 88) advocates the use of sodium pyrosulphate, but, after trial of both, my preference is for the potassium salt.

into solution by prolonged digestion with hot concentrated hydrochloric acid, and subsequent repeated evaporations with sulphuric acid. This method is, however, very tedious, and the solution is apt to be incomplete, so that the method described below should always be adopted. It depends on the setting free of sulphur trioxide on fusing potassium pyrosulphate, this forming soluble sulphates with the oxides present.

Into the crucible containing the ignited precipitate about 5 to 10 grams of coarsely powdered acid potassium sulphate are poured. This salt should have been previously fused so as to be free from water of crystallization and reduced to the pyrosulphate condition. The amount used will naturally vary with the weight of the precipitate, but the limits mentioned will be ample in any case. In general, it is hardly necessary to weigh out the exact amount of acid sulphate, but to put in enough to fill the crucible about one-third, or somewhat more if the precipitate weighs over 0.30 gram. In pouring in the salt, care should be taken that none of the light ash or oxide powder is expelled and lost.

The crucible is placed over a low flame, that of a small glass alcohol lamp serving the purpose admirably, and heated gently till the salt is fused. It is then raised to a distance above the flame (about a foot or so), where the pyrosulphate will remain in a state of fusion and the moisture which it contains will be driven off, without any boiling or spattering against the crucible cover. With some practice the height can be adjusted easily, and this point is an important one to attend to, as any drops on the cover or the upper sides tend to spread on further heating and run over the edges, leading to loss of iron. The whole process at this stage must be carefully watched at intervals, therefore, to guard against such a mishap.

In the course of half an hour or so any water will be driven off, and the crucible can be lowered gradually till immediately above the small flame, where it is kept for another hour or so. Here also the contents should be watched to see that there is no spattering. The precipitate has been gradually dissolving.

and the fused salt become darker in color. The larger lumps stay at the bottom, while a considerable part floats on the top of the liquid.

When the greater part of the floating portion has dissolved, any small particles which may be adhering to the sides above the level of the liquid may be washed down by a slight rotary motion of the crucible, and the flame is turned up, or a Bunsen burner substituted for the alcohol lamp. This more intense heating should be carried out with caution to avoid boiling, and, until the last stages, the bottom of the crucible should not be allowed to become red-hot. White vapors of sulphur trioxide are given off, and the crucible is examined every now and then till all the floating precipitate has been dissolved. If any particles obstinately adhere above the liquid, the crucible may be held obliquely in the triangle, so as to let the fused salt act on these.

The heat is then increased somewhat till the bottom of the crucible is a faint red, the liquid getting thicker through loss of sulphuric acid and the formation of the more difficultly fusible normal potassium sulphate. The liquid mass becomes also a very dark brown, almost opaque if considerable amount of iron is present, the depth of color increasing with the temperature. This is due to the greater dissociation with increasing temperature, and the consequent larger proportion of yellow or brown iron ions. The bottom of the crucible may be examined, notwithstanding the opacity of the liquid, to see if all the precipitate has been dissolved, by removing the flame, and allowing the crucible to cool with the cover off. The fused mass will gradually become less opaque and lighter in color, till it is transparent enough to be seen through before solidification commences at the surface.

When no more undissolved substance is visible, the heating at a low red heat is continued for ten minutes or so, to render complete solution certain, and the crucible is placed on a stone or iron slab to cool. This cake loosens from the crucible far

more readily than that of fused alkali carbonates, and also usually cracks, so that it offers no difficulty in its removal.

It may seem that this process calls for almost constant attention and that it takes an inordinate amount of time. In reality, however, after one has had a little practice in adjusting the heat at the various stages, only an occasional glance is necessary, and the whole can often be accomplished in from three to four hours, especially if macerated paper has been used, so that the oxides are in the form of a powder. This, however, is of no great importance, as the analyst can be busy with other parts of the analysis.

When the sulphate is cold, water is poured in to about half fill the crucible, and it is gently heated till the cake loosens, when this is transferred by means of the platinum spatula to a 250-c.c. beaker. The crucible is well washed with hot water into the same beaker, until all adhering sulphate is removed, and the cover is treated likewise. The final volume of liquid in the beaker may be about 100 c.c. About 10 c.c. of concentrated sulphuric acid are added, not only to facilitate the solution, but to prevent reversion to or precipitation of metatitanic acid, which would diminish the apparent amount of titanium dioxide as determined later by the colorimetric method (Dunnington). The beaker is then heated over a low flame till solution is complete, except for traces of silica, which is practically insoluble in the melted potassium pyrosulphate.

The contents of the beaker are filtered through a 7-cm. filter into a 250-c.c. beaker, the first beaker being well rinsed at least half a dozen times, and the filter also well washed. If the fusion has been successful but a few flakes of silica will be found in the filter. If not it will also contain small, dark particles of undissolved oxide.

In any case, it is placed in an unweighed, small crucible, carbonized at a gentle heat, ignited and weighed. A drop of dilute sulphuric acid and two or three of hydrofluoric acid are added, driven off by gentle heating, the crucible again ignited and weighed. The loss in weight represents the trace of silica,

which is to be added to that of the main portion, already determined (p. 96). It will seldom amount to more than a milligram or two.

The residue left in the crucible, which will contain a little iron or titanium oxides, is dissolved by fusion with a small lump of acid potassium sulphate, which is quickly effected. After cooling, this is dissolved in the crucible in a little warm water containing a drop of sulphuric acid, and any barium sulphate and possible platinum filtered off through a 5½-cm. filter. This is ignited in a small crucible, the barium sulphate floated off from the heavier platinum, collected on a small filter, ignited and weighed, and its weight deducted from that of the ignited ammonia precipitate. This procedure will only be necessary if persulphate has been used in the ammonia precipitation, and then only if there is a notable amount of barium in the rock. The small bulk of filtrate is to be added to the main filtrate in the 250-c.c. beaker.

Reduction of Ferric to Ferrous Iron.—The filtered solution of the mixed sulphates contains all the iron in the ferric state. This has to be reduced to ferrous for titration with potassium permanganate, to determine the total iron. As has been previously noted (p. 69), the use of zinc for this purpose is not to be recommended, and the best reagent is hydrogen sulphide. This commends itself on account of its certainty and rapidity of action, its easy and complete removability, and still more by the fact that it has no reducing action on the titanic sulphate present.

A current of this gas, of course washed with water, is allowed to bubble at the rate of a bubble a second, through the solution in the 250-c.c. beaker, which is covered with a 4-inch watch-glass, the gas being introduced through a bent glass tube, passing through the lip and reaching to the bottom. Although Hillebrand recommends that the solution be hot, I have not found this necessary, and pass the gas through the cold solution. The current is continued till reduction is complete, which is indicated by the liquid becoming turbid and masses of sulphur

separating, which are stained brown by traces of platinum sulphide. At least fifteen minutes should be allowed for this, as, if the reduction is incomplete, the amount of total iron will be too low, and that of alumina too high.

The glass tube through which the gas has been introduced and the cover glass are rinsed off into the beaker, and the contents are filtered off through a 7-cm. filter into a 400-c.c. flask. This is to be done as quickly as possible, and the filter kept full. The washing is carried out with water containing some H_2S, six or eight rinsings of the smaller flask and passage through the filter being sufficient. Owing to the presence of finely divided sulphur, the filtrate is always opalescent. But this need cause no concern, as it is completely oxidized by the sulphuric acid present in the subsequent boiling, and the liquid becomes perfectly clear.

The solution of the small cake of fused sulphate containing the residue from the trace of silica is poured in if it has not been added before, and the crucible washed once or twice, the the excess of H_2S present being more than sufficient for the complete reduction of the ferric sulphate which it contains. A half dozen small pieces of platinum-foil, bent at right angles, are dropped in to prevent bumping, and a square piece of platinum-foil, through which holes have been cut, is placed over the mouth of the flask and fixed in place by bending down the corners.

The flask is then placed over a flame, and a carbon-dioxide generator set in action, the gas being freed from possible H_2S (due to sulphides in the marble) by passing through a column of pumice soaked in copper sulphate solution, and washed by a wash-bottle containing water. The CO_2 is allowed to bubble at the rate of several bubbles a second, and is passed into the flask above the liquid by a short piece of glass tubing inserted through one hole in the platinum-foil. Complete saturation by H_2S is shown by small bubbles of this gas rising in the liquid soon after the heating begins, and long before it has become hot enough to simmer or boil.

When boiling has begun, the flow of carbon dioxide is still kept up, and the boiling continued briskly until the expulsion of H_2S is complete, as shown by occasional testing of the steam issuing from the second hole with filter paper dipped in lead acetate solution. This process will take about 20 minutes, unless much opalescent sulphur is present, when possibly half an hour will be needed to clear the liquid. There is no danger of reoxidation of the ferrous sulphate, since at first the liquid contains hydrogen sulphide, and later the boiling is carried on in an atmosphere of steam and carbon dioxide.

The flask is next removed from the flame, and, while the current of CO_2 is still passing, is placed in a basin or other receptacle and cooled quickly in a stream of water up to the level of the liquid contents, the current of CO_2 passing the while.

Titration of Iron.—When the contents of the flask are quite cold, it may be emptied into a 600-c.c. beaker, and rinsed out several times with the cold, boiled water. The pieces of platinum-foil are allowed to drop into the beaker, and the foil cover and tube for the introduction of CO_2 are also washed.

The contents of the beaker (best placed on a square of white porcelain or paper) are then titrated with the standard solution of potassium permanganate, a burette with a glass cock, of course, being used, this having previously been made ready. The preparation and standardization of this solution are described on p. 39. The liquid is constantly stirred till it is just tinged a permanent red, and, as it is clear and colorless, the exact point can be struck with great accuracy. Toward the end the drops must be added one at a time.

The titration may also be carried out in the flask itself, a method recommended by Hillebrand and now adopted by myself, as it keeps the volume of liquid down and is equally accurate. There is also less chance of oxidation, as the titration takes place in an atmosphere consisting largely of carbon dioxide. For this, the flask with its cooled contents, standing on a white porcelain plate, is placed beneath the burette tip, and the permanganate dropped on slowly directly into the

liquid, not running down the sides of the flask. The flask is given a slight rotary motion with the left hand, so as to distribute the permanganate and lessen the chance of splashing. If any drops fall or are splashed on the upper sides they are washed down into the flask with the cold boiled water. With a little practice the proper manipulation is easily learned and the titration quickly carried out.

When the amount of standard solution needed is roughly known, about half of this may be added quickly in portions of 1 or 2 c.c. at a time, with stirring to disappearance of the color after each addition. Beyond this, the permanganate should be added by drops, with constant stirring, to avoid overrunning the mark. When the color begins to disappear slowly, single drops are to be added with great caution, till one of them produces a pink blush throughout the liquid which does not vanish on stirring or rotating for a short time. As very dilute solutions of permanganate are unstable, this color will vanish on standing, even when the reaction is complete. After waiting a few moments after the addition of the last drop, the burette is read off to the nearest tenth of a cubic centimeter.

The number of cubic centimeters of permanganate solution used is then multiplied by the amount of Fe_2O_3 equivalent to 1 c.c. of the standard, the product giving the total iron in the rock determined as Fe_2O_3. From this is to be deducted the iron present as FeO, and that which may exist as FeS_2, which will be determined later.

After titration of the iron, if the amount of TiO_2 is less than 2 per cent, the solution is to be evaporated on the water-bath down to about 150 c.c., either in porcelain or platinum, the beaker being rinsed well and the rinsings, added during the evaporation. This liquid is to be placed in a 250-c.c. measuring flask, with glass stopper, but not filled to the mark, and reserved for the determination of titanium dioxide.

5*d*. Titanium Dioxide.

The Test Solution.—For the determination of this constituent the whole bulk of solution in which the total iron has been titrated is best adapted. This contains all of the titanium in solution as sulphate, and with no possible traces of hydrofluoric acid, which exerts such a deleterious effect on the colorimetric method. If, for any reason, this solution is not available, the TiO_2 can be determined in a separate portion of rock powder, which is brought into solution by evaporation (under the hood), in a platinum crucible with a mixture of dilute sulphuric acid (1:1) and hydrofluoric acid. This is continued till fumes of sulphuric acid are given off, but not to dryness, when more of the dilute sulphuric acid is added, and the evaporation continued till there are no traces of hydrofluoric acid,* which may take four or five repetitions and additions of sulphuric acid. Or the solution in which ferrous oxide has been determined will answer, if it is evaporated down (in platinum) repeatedly with sulphuric acid, to expel hydrofluoric acid completely.

There are two very distinct methods—gravimetric and colorimetric—by which titanium dioxide may be determined. The latter is by far the most accurate and expeditious, and is the one which is adopted by the chemists of the U. S. Geological Survey, and which I also employ. It will therefore be described first in some detail, the gravimetric methods being discussed later more cursorily, for the benefit of those who may not have the applicances necessary for the colorimetric work.

Colorimetric Method.—This method, which was first proposed by Weller,† depends on the yellow to brown coloration of solutions of titanic acid by hydrogen peroxide, TiO_3 being formed, the depth of tint on complete oxidation being proportional to the

* Cf. T. M. Chatard, Bull. U. S. Geol. Surv., No. 78, p. 87, 1891; W. F. Hillebrand, Bull. 176, p. 69; Bull. 305, p. 116.

† Weller, Ber. Deutsch. Chem. Ges., XV, p. 2593, 1882. Cf. Hillebrand, Bull. 176, p. 67; Bull. 305, p. 110.

amount of TiO_2. Vanadium, molybdenum and chromic acid interfere with the method, the first two through a similar coloration of their solutions by H_2O_2, and the last by the normal color of solutions of chromates. It is seldom, however, that any of these elements are present in rocks in sufficient amount to affect the method seriously. Hillebrand has shown that HF, even in traces, has a very marked effect in preventing the coloration, either partially or wholly. It is absolutely necessary, therefore, that every trace of hydrofluoric acid be driven off from the solutions used, and that the hydrogen peroxide be free from it. This is not always true of all commercial brands, so that that which is used should be tested for fluorine before using.*

The essentials for the colorimetric method are a standard solution of titanium, containing 0.001 gram of TiO_2 per c.c., and a pair of glass vessels with parallel sides which are the same distance apart in each, although a good pair of Nessler tubes or Schreiner's colorimeter can be substituted for these.

The preparation of a standard solution of titanium is somewhat awkward, owing to the difficulty of obtaining pure titanium compounds, and the necessity for driving off all hydrofluoric acid, without the use of which the solution of titanium compounds is difficult. If potassium fluotitanate can be procured, a definite weight of this is to be evaporated repeatedly with sulphuric acid, but not to dryness, the final solution being made up with water to a volume necessary to give it the required strength of 0.001 gram of TiO_2 per c.c., enough sulphuric acid being added to bring the final strength of this up to 5 per cent. This is the method adopted in the Geological Survey laboratory.

The solution can also be made from titanium dioxide itself, which can be obtained reasonably pure from some makers. This can be brought into solution by fusion with acid potassium sulphate, acting on very small quantities at a time (about 0.10 gram), the fusion being prolonged and conducted with care to

* Hillebrand, Jour. Am. Chem. Soc., XVII, p. 718,. 1895; Bull. 305, p. 36.

avoid loss. Or the solution can be somewhat more readily effected in quantity by evaporation first with sulphuric and hydrofluoric acids, and then repeated evaporations with sulphuric acid alone, which is the method I have employed. A sulphate of titanium of reasonable degree of purity is also sometimes obtainable, and this can be brought into solution in the same ways.

Iron is the chief impurity in the titanium compounds as usually procurable, and, although present in small amount as Fe_2O_3, it is best to determine it in a definite volume of the titanium solution, so as to arrive at the correct figure for TiO_2. This should be done before the solution is diluted finally to the standard strength, but the volume must be known. The method used for determining ferric oxide may be used, 100 c.c. of the solution being reduced by H_2S, the latter driven off by boiling, and the solution titrated. For all but the most accurate work, however, the amount of impurity will be so small that this determination of iron and correction for it may be neglected. It will not be necessary if potassium fluotitanate has been used.

However prepared, the amount of titanium in the solution should be determined, in a definite portion of 50 or 100 c.c., by precipitation with ammonia and weighing the ignited precipitate of TiO_2. If iron is present correction must be made for this, as Fe_2O_3, based on the determination just given. The solution is then to be diluted to the required strength.

As to the glass vessels used, the type recommended by Hillebrand is preferable to Nessler tubes. It is absolutely essential that two opposite sides in each be parallel, and the distances apart be identical, certainly within 1 per cent of the distance. The other two sides need not be parallel, but should be blackened on the outside to exclude light. Those used by me are 12 cm. high, and 4 cm. between the parallel sides each way, measured internally, and were procured from Eimer & Amend.

It seems to be a difficult matter to obtain such glasses in this country, or at least to find them in stock, though they can be imported from abroad. They are best made of glass plates

cemented with a material which will resist the action of dilute acids. One can make them by cutting plate glass (2 to 3 mm. thick) in the requisite shapes and cementing them with Canada balsam, the angles being strengthened by narrow strips of rubber tape fastened with a rubber cement. Or a suitable pair may be made, as Hillebrand suggests, from a couple of square 4-oz. bottles. Two opposite sides of each are to be ground off until the calipers show that they are of equal dimensions and parallel. The upper part is sawed off just below the shoulder, and plates of glass cemented on with Canada balsam.

The use of a suitable box is necessary to exclude side-lights, and render the comparison more delicate. An appropriate form is illustrated by Hillebrand (op. cit., p. 70). This may be conveniently made from a box in which the ceresine bottles containing one-half pound of hydrofluoric acid are packed, if the glasses do not measure over 4.5 cm. in width.

The box measures $20 \times 9.5 \times 9.5$ cm. internally. The square bottom is first removed, leaving the box open at either end. For the sliding cover a 3-inch plate of ground glass is substituted, this slipping snugly into the cover grooves, which may need a little widening with a penknife. About 5 cm. of the side next to the free edge of the glass is cut away, to allow the insertion of the glasses. This side now becomes the top of the box. A thin wooden partition (made of cigar-box board), provided with two rectangular openings corresponding to the glasses, may be inserted on the near side, and held in place by a few light brads, though I do not find that this partition is necessary. A narrow slot is cut clear across the top of the box alongside the partition, and the cover of the box used to make a shutter which will slide stiffly up and down, so as to remain at any desired height. The box and partitions are blackened inside and out, and the result is a box which is light and compact enough to be held easily in the hand.

The actual process is as follows: The solution of the rock powder in which the TiO_2 is to be determined, and which we will call the test solution, is evaporated down, if necessary, to an

appropriate volume, and placed in a measuring-flask of suitable size with glass stopper when cold. Sufficient hydrogen peroxide is added to oxidize the TiO_2 completely, 5 to 10 c.c. being ample in most cases, and the whole is diluted to the mark and well mixed.

The volume of liquid depends on the amount of TiO_2 present, 250 c.c. being suitable for the majority of rocks, in which the percentage of TiO_2 is less than 1. In rocks like granite or rhyolite, where the amount is very small, a volume of 100 c.c. is preferable. In basic rocks, containing more than 1 per cent of TiO_2, the volume should be increased proportionally, 500 c.c. being appropriated if the percentage is from 1 to 2, and 1000 c.c. if it is from 2 to 4. It is essential to have the depth of color in the test solution less than that of the standard solution diluted as described below. Instead of using 500-cc. or 1000-c.c. flasks, 25 c.c. of the 250-c.c. volume of the test solution can be diluted with 25, 50 or 75 c.c. of water in the test-glass.

It must be noted that the delicacy of this method is greater when the color is not very deep, so that, when much TiO_2 is present, the dilution should be large. The most favorable tint is a rather deep straw-color, about that of light beer. Stated quantitatively, a favorable strength is when the solution contains approximately .00002 to .00003 gram of TiO_2 per c.c., that is, when 10 c.c. of the diluted standard solution mentioned below has to be diluted with from 40 to 20 c.c. of water to bring it to equal tint with the test solution.

An indeterminate quantity of the test solution is poured into one of the glasses, say the left-hand one. Or if great dilution is necessary, as mentioned above, 25 c.c. of the solution made up to 250 c.c. is measured into the glass, and this diluted to the requisite light tint by the addition of 25, 50 or 75 c.c. of water, amounting respectively to a total volume of test solution of 500, 750 or 1000 c.c.

Ten c.c. of the standard solution, containing 0.01 gram of TiO_2, is placed in a 100-c.c. measuring-flask, provided with a glass stopper, 5 c.c. of hydrogen peroxide added, diluted with

water to the mark and well mixed. Each c.c. of this diluted standard will then contain 0.0001 gram of TiO_2. This amount of diluted standard will suffice for the determinations in three rocks, and if this quantity is not required 5 c.c. of the standard may be taken, and diluted to 50 c.c. after addition of H_2O_2. The color disappears after a time, so the diluted standard must be made up fresh for each determination or batch of determinations. It is evident that the color cannot be restored by addition of H_2O_2 to a solution already diluted to the mark, as this will increase the volume of liquid and so lessen the amount of TiO_2 per c.c. If a series of rock analyses is being made it is well, to economize the standard solution, to make the titanium determinations in batches of three rocks at a time, the earlier test solutions being kept in suitable flasks, but not diluted to the mark, until the determination is to be made.

Two burettes are fixed in a stand, and the one filled with the diluted standard, the other with water, the position of the meniscus in each being noted. Ten c.c. of the diluted standard are then run into the right-hand glass, and water added from the other burette, in small quantities at a time, the color of the two being compared after each addition. The shutter should be slid down till only the liquid in each glass is visible, and none of the empty portion above. As the color of the diluted standard approaches that of the test solution, the addition of water should be cautious and by a few drops at a time, till the point of agreement is reached, when the amount of water added is read off and noted down. During this addition of water the box with the glasses is gently shaken so as to mix the liquids, or the test solution is gently stirred with a glass rod flattened at one end (Hillebrand). Great care must be taken not to break the glasses. Ten c.c. of diluted standard are then again run into the right-hand glass, this having been previously emptied, and water added as before, the water burette being refilled if necessary. This operation is repeated a third time, so as to furnish a mean of three determinations, which should not vary more than 1 c.c. from each other. In adding the water the

second and third times it is well to cover the burette with a roll of paper held in place by an elastic band, so as to avoid any bias produced by a knowledge of about the amount of water which is to be added to make the second and third observations like the first.

When observing the color after each addition of water, the box is held in the hand toward a good light, as that of a window, if possible, without the disturbing effect of sunlit foliage outside. The operation is best carried out in the daytime, as distinctions in the shades of color are thus much more readily discernible than by artificial light. It will be found advantageous to rest the eyes occasionally by looking at the floor or a dark corner, as their sensitiveness is apt to diminish through fatigue.

When testing the method with known amounts of TiO_2 for the first few times I noticed, in my own case, a tendency to consider that the colors matched some time before they actually should have done so. Any such tendency, or the reverse, which may be true of others, is to be guarded against. After a little practice one soon becomes expert in judging of exact agreement and in arriving at concordant results. This practice is best obtained by making up test solutions from small measured volumes of standard diluted with varying known volumes of water, and determining the TiO_2 in these. As the amount of TiO_2 is known, one has a check on the personal equation, and will soon be in a position to determine unknown quantities of TiO_2. For one who has never used the method, this preliminary practice must not be omitted.

An example of the simple calculation necessary is given elsewhere (p. 186), the underlying principle being that, as the colors of the two solutions are the same, the amount of TiO_2 per c.c. is equal in both. This amount is known from the diluted standard solution diluted with a known bulk of water, and it only remains to multiply this amount of TiO_2 per c.c. by the volume of the test solution to arrive at the weight of TiO_2 in the portion of rock powder taken, and hence its percentage. As the whole of the titanium dioxide has been thrown down

with the alumina, the amount of the former is to be subtracted from the weight of this ignited precipitate to arrive at the weight of the alumina.

If the rock contains much iron, the test solution will be slightly colored by the presence of ferric sulphate, and in the most accurate work a correction is to be applied for this. Hillebrand has shown that this will amount to a deduction of 0.02 per cent from the apparent percentage of TiO_2 if 10 per cent of total iron as Fe_2O_3 is present, and in proportion for larger quantities. In most cases, however, this correction may be neglected.

If the glasses described above are not available, and it is desired to use Nessler tubes, the method is modified as follows, according to the plan of Prof. Penfield. A light box is used of such dimensions as to snugly hold the two tubes side by side. These rest either on a ground-glass plate forming a false bottom, or on a horizontal wooden partition with holes or a broad slot cut so as to admit light from below. Beneath this or the ground-glass plate a mirror is fixed at an angle of 45° above the real bottom, admitting light from a side-opening and transmitting it vertically up through the tubes.

The test solution is prepared as above, but the standard is used undiluted. One Nessler tube is filled with the colored test solution up to the 50-c.c. mark, and in the other is placed 5 c.c. of hydrogen peroxide, which is diluted with a known volume of water nearly up to the same mark. The standard solution is then added in very small quantities at a time from a burette, the liquid being stirred, and the colors observed after each addition, till there is agreement between the two. With a little practice, and knowledge of the approximate amount of titanium present in the rock, the heights of the two solutions can be made sensibly identical, but several determinations are always advisable. In this case, the Nessler tube for the standard solution is to be emptied and washed carefully each time.

While this modification involves the use of more easily obtainable glass vessels, as well as less standard solution, it is not quite as accurate as the other, although sufficiently so for most

purposes, and far more so than the gravimetric method commonly adopted.

Another alternative apparatus is that of Schreiner, described by Hillebrand.* This consists essentially of two graduated glass tubes to hold the test and diluted standard solutions, the liquids being examined vertically. The depths of the two columns of liquid are changed by means of two smaller glass tubes with flat bottoms immersed in them, the graduated tubes being moved up or down until the shades are identical. The strengths of the two solutions are inversely as the heights of the columns. This apparatus is said to give good results, and may be purchased from Eimer & Amend. A new form of colorimeter which has recently been described by G. Steiger † utilizes the same principle.

Gravimetric Methods.—Although the colorimetric method is by far the simplest and most expeditious, is capable of extreme accuracy, and is applicable in the great majority of rocks, it is not so well suited to rocks or minerals which contain more than about 5 per cent of TiO_2, because of the loss in delicacy with the great depth of color, and the possibility of serious error with large dilution necessary to overcome this. Occasion may therefore arise for the determination of titanium by gravimetric methods. While the use of these is not advised, if the colorimetric method is suitable, they may be briefly discussed.

The best gravimetric method is that of F. A. Gooch,‡ which is fully described by Hillebrand,§ to whom the reader may be referred. While rather complicated, it is very accurate, although Hillebrand has shown that it is not to be used when zirconia is present in the rock.

A simplified modification of this, due to Prof. H. Fay, is described by C. H. Warren¶ and is stated to be "highly satisfactory, both in point of simplicity and accuracy."

* Hillebrand, Bull. 305, p. 33.
† Jour. Am. Chem. Soc., Vol. XXX, 1908, p. 215.
‡ F. A. Gooch, Bull. U. S. Geol. Surv., No. 27, p. 16, 1886.
§ Hillebrand, Bull. 176, p. 71; Bull. 305, p. 113.
¶ Am. J. Sci., XXV, 1908, p. 23.

"Fuse 0.4-0.6 gram of finely ground ore with 6-8 times its weight of mixed alkali carbonates until action ceases. Extract the mass with hot water, and decant the solution through a filter. Boil the residue with 25 c.c. of sodium carbonate solution, filter and then wash the residue on the filter paper several times with dilute sodium carbonate solution. Place the filter and residue in a platinum crucible and ignite at a low temperature until the filter paper is burned. Fuse with 12-15 parts (5 to 9 grams) of dry acid potassium sulphate for one-half hour. The temperature of the fusion should be so regulated that the mass is kept in the molten condition, but sulphur trioxide should escape only when the lid of the crucible is removed. Cool and remove the fusion from the crucible by means of a long platinum wire, which has been inserted in the fused mass. Suspend the fusion in 200 c.c. of cold water to which has been added 100 c.c. of sulphurous acid and allow to stand in a cool place until solution is complete.

"Filter if necessary. To the solution add 125 c.c. acetic acid (sp.gr. 1.04) and dilute to 800 c.c. in a liter beaker. Add 20 grams of sodium acetate dissolved in a small amount of water and boil from 3-5 minutes, adding *just before the boiling-point is reached* an additional 25 c.c. of sulphurous acid. Allow to stand in a warm place for one-half hour and then filter by means of a siphon through a 9 cm. paper.

"Wash the precipitate with 5 per cent acetic acid solution until most of the sulphate has been removed, and then ignite the paper and precipitate. Fuse with acid potassium sulphate again. Proceed exactly as before, finally igniting and weighing the precipitate as TiO_2."

Warren states that in two determinations 0.01 per cent of iron could be detected in the precipitate and that probably the same amount of alumina and manganese are included. For very accurate work a third precipitation is advisable. In a letter he lays stress on the importance of adding the additional 25 c.c. of SO_2 just before the boiling begins.

An approximate determination of TiO_2 may be made in the

solution after the titration of total iron by an old and well-known method. This consists in diluting the solution in a 1000-c.c. beaker to about 500 c.c., adding ammonia or solution of sodium carbonate till a permanent precipitate just forms, then 4 c.c. of concentrated sulphuric acid and 100 c.c. of solution of sulphur dioxide, diluting to 750 c.c. and boiling for several hours, the water lost by evaporation being replaced with hot water containing SO_2 added from time to time. The titanium is precipitated as metatitanic acid, collected on a filter, ignited and weighed as TiO_2.

As thus precipitated, the TiO_2 is almost always contaminated by notable amounts of alumina and ferric oxide, which fall with it, and the operation should be repeated, after bringing the ignited precipitate into solution by fusion with acid potassium sulphate and solution in hot water containing some sulphuric acid. It may happen, on the other hand, that the precipitation of titanium is incomplete, if the liquid contains too much free acid. Another source of error is the tendency of the precipitated metatitanic acid to adhere firmly to the sides of the beaker, from which it is removable with great difficulty or only in part. With such serious defects, and in view of its tediousness, the use of this antiquated method should be abandoned.

5*e*. Manganese and Nickel Oxides.

If the basic acetate method has been used, and it is desired to determine manganese in the main portion, it may be done according to the following method, which is that of Hillebrand.* I no longer use this, however, but determine manganese in a separate portion by the colorimetric method (cf. p. 167).

The combined filtrates from the precipitate of alumina, iron, etc., if the basic acetate method has been used, are evaporated down to a bulk of about 100 c.c., best in the platinum basin, after ammonium water has been added to alkaline reaction.

* Hillebrand, Bull. 176, p. 60; Bull. 305, p. 97.

This will in almost all cases produce a precipitate of aluminum and ferric hydroxides, which must be filtered off on a small filter. It is at this point that there is danger of neglecting to collect the slight precipitate of alumina, if the manganese is precipitated without previous filtration, so that any alumina or iron present is weighed with it.

The filter is ignited in the crucible which is used for the ignition of the main precipitate of these oxides (see p. 105). The filtrate is caught in a 200-c.c. flask. and if the platinum basin is stained brown by deposited manganese, this is to be dissolved in a few drops of hydrochloric acid and a drop of sulphurous acid and washed into the flask.

Enough ammonia water is added to make the contents of the flask strongly alkaline, and a current of H_2S is passed through it for ten minutes, which precipitates the manganese, and also nickel, cobalt, copper and zinc, or part of the platinum which may have been derived from the basin. The flask is corked and allowed to stand for twenty-four hours.

The precipitated sulphides are collected on a 7-cm. filter, and washed with water containing a little ammonium chloride and ammonium sulphide, the flask being also rinsed out with this. The filtrate is received in a 400-c.c. beaker, and reserved for the determination of lime and magnesia (p. 126).

The sulphide of manganese (and zinc) is dissolved by passing a few cubic centimeters of hydrogen-sulphide water acidified with one-fifth of its bulk of hydrochloric acid through the filter, and washing several times. The liquid is received in a small porcelain or platinum basin and evaporated to dryness. A few drops of solution of sodium carbonate are added and the contents of the dish again evaporated to destroy ammonium salts, which would hinder the complete precipitation of manganese. The dry salts are then dissolved in about 10 c.c. of water to which a few drops of hydrochloric acid are added, and are precipitated with sodium carbonate. The manganese carbonate is collected on a 5½-cm. filter, washed, ignited in a weighed crucible and weighed as Mn_3O_4.

The black residue on the filter may contain nickel, cobalt, copper and platinum. The filter is incinerated in a porcelain crucible, and dissolved in a few drops of aqua regia, evaporated to dryness in the crucible, dissolved in a little water and hydrochloric acid, and a little strong hydrogen-sulphide water added, which will precipitate the copper and platinum. These are filtered off on a small filter, and in the filtrate, to which ammonia is added, nickel and cobalt are precipitated by hydrogen sulphide. A few drops of acetic acid are added and the liquid allowed to stand for some hours, when the nickel (and cobalt) sulphides are caught on a 5½-cm. filter, ignited and weighed as oxide. The amount of cobalt is so small in terrestrial rocks that it is not necessary to separate it from the nickel, but its presence may be established, if desired, by testing the oxide with the borax bead.

It is, however, almost always best to determine nickel and copper in a separate portion, as described on page 181.

5*f*. Lime and Strontia.

Lime.—For determination of lime the filtrate from the precipitations by ammonia (p. 104), or if manganese has been determined, that from the precipitate of manganese sulphide is used. In the last case the ammonium sulphide need not be destroyed. The filtrate should not amount to more than 500 or 600 c.c., and is held in an 800-c.c. beaker. If much more than this, it is advisable to evaporate it down to 500 c.c., but this should not be necessary if care has been taken to avoid unduly large quantities of washing-water.

In a series of analyses of volcanic rocks this filtrate, from precipitation by ammonia alone, showed a slight but noticeable greenish tinge in nearly all the basaltic rocks. This was found to be due to the presence of nickel, the basalts containing abnormally large amounts of this, up to 0.30 per cent. In dealing with basic rocks it will be well to be on the lookout for this

coloration, as it will indicate the advisability of determining nickel. Its presence will not interfere with the rest of the analysis, since the liquid is strongly ammoniacal from this point on, and the nickel will be held up in solution and will not contaminate the lime and magnesia.

A little ammonium is added till the liquid smells slightly of it, and the liquid brought to a boil. In the meantime 1 gram or so of ammonium oxalate is dissolved in 25 to 50 c.c. of water, with the aid of a gentle heat, and is poured into the large beaker when the liquid begins to boil. The boiling is continued for a few minutes, and the beaker allowed to stand for an hour.

The liquid is then filtered through a 7- or 9-cm. filter, according to the amount of calcium oxalate, the filtrate being received in a 1000-c.c. beaker. As little as possible of the precipitate is allowed to pass onto the filter, and this and the beaker are washed only two or three times with warm water.

About 50 c.c. of warm dilute (1:5) nitric acid are prepared in a small beaker, the 1000-c.c. beaker with the filtrate removed from beneath the funnel, and the 800-c.c. beaker in which the lime has been precipitated substituted for it. The filter is then filled with the dilute nitric acid, which, when it begins to drop through, is allowed to fall upon the sides of the beaker, held obliquely, at the upper line of adhering calcium oxalate. The beaker is turned round so that the acid may flow over and dissolve every part of the adhering precipitate, a little being also dropped on the stirring-rod. This operation is repeated two or three times, till the whole of the precipitate is dissolved, that which may be on the filter as well as that in the beaker. The filter is then well washed with water, for which six or eight times suffice, the washings being caught in the 800-c.c. beaker, of course.

After rinsing down the sides of the beaker, a few drops of ammonium-oxalate solution are added, and the acid liquid is neutralized with ammonia water till it smells rather strongly of this gas. The small bulk of liquid, which should not be more than an inch or two in depth, is then brought to a boil, allowed to stand for a short time, and filtered through the same filter, the

filtrate being received in the 1000-c.c. beaker which contains the filtrate from the first precipitation. All the calcium oxalate must, of course, be transferred to the filter, and that which adheres to the sides be removed by rubbing with a stirring-rod tipped with a short piece of rubber tubing, and also washed into the filter. A few washings only will suffice, and it will be necessary to catch only the first of these in the beaker along with the main bulk of filtrates.

It must be noted in the case of such fine precipitates as those of calcium oxalate and ammonium-magnesium phosphate, that they have a very strong tendency to creep up the wetted surfaces of their receptacles. Great care must therefore be taken in dealing with them to examine the whole surface of the beaker, so that no patches may escape the rubber-tipped rod, and also to wash them into the filter with a fairly strong stream of water from the wash-bottle, which will overcome the surface tension of the liquid adhering to the sides and which tends to hold them back.

This double precipitation is necessary, since the calcium oxalate first thrown down carries with it some sodium salts, as well as some magnesium. Precipitation at a boiling heat is preferable to that in the cold, both because it is more complete, unless the liquid is allowed to stand for a much longer time, and also because the crystalline precipitate is larger grained and hence less liable to pass through the filter-paper.

The filter containing the precipitate is placed moist in a medium-sized platinum crucible, which has been previously strongly ignited and weighed, and is heated gently to dryness, the paper carbonized and then incinerated at a higher temperature, and finally blasted for about ten minutes. This converts the calcium carbonate to oxide, as which the lime is weighed, with as little delay as possible after cooling in the desiccator. It is always a wise precaution, especially if the amount of precipitate be considerable, to blast once more after weighing, to see that a constant weight is obtained.

With a good Bunsen burner, as Hillebrand* points out, the calcium carbonate, at least in the amounts usually found in igneous rocks, can be converted to oxide without blasting. But this takes considerably more time, and the use of the blast will usually be safer.

Strontia.—The calcium oxide, as thus prepared, contains the strontia of the rock, but scarcely ever more than traces of baryta.† If it should be desired to determine the former, it may be done, or at least the operation may be commenced, immediately after the final weighing of the lime.

While the amount of this constituent is always very small, in almost every case less than that of barium, yet its determination involves so little trouble and loss of time, that it is to be desired that it be done more frequently than is now the case. At the same time, if the amount of lime is less than 1 per cent or so, it will scarcely be worth while to do this, except for very exact analyses. The method to be employed depends on the solubility of calcium nitrate in a mixture of absolute alcohol and ether, and on the insolubility of strontium nitrate in this medium.

After the final weighing, and before it has had time to absorb an appreciable amount of carbon dioxide from the atmosphere, the lime is transferred to a 4-inch test-tube by emptying on a small piece of glazed paper and pouring into the tube. A few drops of water are added and the lime completely slaked, and then a few drops of concentrated nitric acid, just sufficient to dissolve the lime completely.

The contents of the test-tube are to be evaporated to complete dryness, which is best accomplished by heating the tube in an air-bath at 135°, the mouth of the tube projecting from one of the upper orifices of the oven. When completely dry and cool, 5 or 6 c.c. of a mixture of ether and absolute alcohol in equal parts are added, the tube corked and laid aside for twenty-four hours with occasional shaking, till the calcium nitrate is entirely dissolved.

* Hillebrand, Bull. 305, p. 102.

† Hillebrand, Bull. 176, p. 63; Bull. 305, p. 222.

The contents of the tube are then to be filtered through a 5½-cm. filter and well washed (six times) with the same mixture of absolute alcohol and ether. The filter is allowed to dry in the funnel, after which the strontium nitrate is dissolved in a few cubic centimeters of water passed through the filter and received in a 50-c.c. beaker, the filter being washed a few times. A few drops of dilute sulphuric acid are added and then alcohol equal in amount to the volume of liquid in the beaker. After standing for twelve to twenty-four hours the precipitated strontium sulphate is filtered off, ignited and weighed. Its weight is multiplied by .56 to obtain that of SrO, and this is deducted from that of the lime.

5*g*. MAGNESIA.

The filtrate from the calcium oxalate contains, of the original rock constituents, only the magnesia and alkalies, with the barium, and part of the manganese and the nickel and other metals of the sulphide group, if these have not been previously determined. There are, of course, also present the alkalies derived from the carbonate fusion and large amounts of ammonium salts. It will not be necessary to remove these last for the determination of the magnesia, which is the only constituent which interests us in this filtrate.

Precipitation.—To the liquid, which may amount to 600 or 800 c.c., and is contained in a 1000-c.c. beaker, 3 grams of hydrogen-ammonium-sodium phosphate (microcosmic salt) dissolved in a little water are added, and 100 c.c. of ammonia water. The mixture is well stirred with a long stirring-rod, and the beaker covered with a large watch-glass and set aside for at least twelve hours, or preferably twenty-four.

At the end of this time the liquid is filtered through a 7-cm. filter, a suction-tube being connected with the funnel. This first filtration is best and quickest carried out with the filter-pump, the filter being supported in the funnel by a perforated platinum cone. The beaker is rinsed out and the filter washed

two or three times with very dilute (10 per cent) ammonia water. Gooch and Austin* have pointed out that the strong ammoniacal water usually recommended (1:3) is entirely unnecessary. It is well, even with the more dilute ammonia, to connect a glass mouthpiece with the wash-bottle by a rubber tube about a foot long, to prevent any injurous effect on the delicate mucous membrane of the mouth. The filtrate and washings are thrown away.

The precipitate on the filter is dissolved in dilute nitric acid (1:5), the acid being caught in the 1000-c.c. beaker and allowed to flow over all the sides of the beaker as far as the precipitate extends, and the filter well washed. The depth of the liquid in the 1000-c.c. beaker should not be more than 3 or 4 cm. A drop or two of sodium-ammonium phosphate solution is added, and then ammonia water till the liquid smells rather strongly of it, and the beaker allowed to stand for an hour.

This reprecipitation is necessary, as Neubauer† and Gooch and Austin‡ have shown that if there is an excess of ammonia, ammonium salts and precipitating phosphate, the magnesium pyrophosphate will not be normal in composition, but will contain an excess of P_2O_5, thus increasing the apparent amount of magnesia. The error will not be of great magnitude in rocks poor in magnesia, as granites and trachytes, where a single precipitation may suffice if the extreme of accuracy is not required, but it may be considerable in more basic rocks. A reprecipitation is therefore always necessary in these, and advisable in those first mentioned.

Filtration in Gooch Crucible.—While the precipitate of magnesium-ammonium phosphate can be collected on a paper filter in the usual way, carbonized from a moist condition and ignited, my predilection is for the use of the Gooch filter, on account of involving a smaller volume of washing liquid, and not leading to possible loss of phosphorus through the reducing action of the carbon of the filter on the precipitate.

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* Gooch and Austin, Am. Jour. Sci., VII, p. 189, 1899.

† Neubauer, Zeits. Angew. Chem., 1896, p. 435.

‡ Gooch and Austin, loc. cit., p. 190.

To prepare the Gooch filter, the perforated crucible is placed in the rubber-covered mouth of the so-called carbon filter, and this is inserted in the rubber stopper of the stout Erlenmeyer flask. The side tubulure is connected with the suction-pump and a gentle aspiration applied. A few cubic centimeters of a cloudy mixture of asbestos and water (p. 41) are poured in, so as to form on complete suction a thin felt on the bottom, which must be completely covered. The felt must not be too thin, or there will be danger of its breaking, nor, on the other hand, should it be inordinately thick, as this will render the filtration unnecessarily slow. For a 25-c.c. crucible, the felt should weigh about 1 or 2 centigrams, when ignited. The felt is washed with a few portions of water, directed gently against the side of the crucible, sucked dry, and the aspiration stopped.

The crucible is heated over a low flame, the bottom cap being left off, and the flame moved about by hand. In this way the felt is well dried without loosening or blistering, as the steam generated from its lower side will escape through the perforations. When quite dry, as is indicated by the whiteness of the asbestos, the bottom cap is put on, and the crucible is covered and ignited at a bright-red heat for a short time, to drive off all traces of water. It is then cooled in the desiccator and weighed.

The Gooch crucible, with the bottom cap and cover removed, is placed in position in the carbon filter, care being taken when inserting it in the rubber mouth, that the latter does not come in contact with the bottom of the crucible and rub off any small pieces of asbestos which may project beyond the perforations.

The suction is then turned on, which should be gentle and at the same time effective, and the liquid is poured slowly into the crucible, the current from the stirring-rod striking the side and not directly on the felt. Otherwise the latter is liable to be torn and some of the perforations laid bare, possibly allowing some of the fine precipitate to pass through. The whole of the liquid is thus filtered, with considerable of the precipitate entering the crucible, so as to protect the felt. The beaker is then rinsed with

a stream of very dilute ammonia water several times, the bulk of the precipitate going into the Gooch crucible. The adhering precipitate is loosened from the sides and bottom of the beaker and from the stirring-rod by means of a rubber-tipped rod, and the last traces of it brought into the filter by gentle streams of the dilute ammonia from the wash-bottle.

The precipitate on the felt is well washed with the same fluid, the crucible being allowed to empty before each addition, of which about half a dozen will be sufficient in most cases. If desired, the washing can be tested by stopping the suction, removing the stopper of the Erlenmeyer flask, and letting a few drops fall on a watch-glass. These are acidified with a drop or two of nitric acid and tested with silver nitrate. It will be well to do this the first few times, till one learns by experience when the precipitate is thoroughly washed.

When the washing is complete the suction is continued for a short time in order to partially dry the precipitate, when it is cut off and the side connection cautiously opened, to avoid any regurgitation of liquid up against the felt. The bottom cap is put on and the covered crucible is heated over a low flame till the precipitate is dry and no more odor of ammonia is perceived. It is then ignited at a bright-red heat for ten minutes, blasting not being necessary. If the mass appears gray it can be rendered white by blasting, or, still better, by moistening with a few drops of nitric acid, drying at a gentle heat, and reigniting.

After cooling in the desiccator the crucible and its contents are weighed, the gain in weight being $Mg_2P_2O_7$. This is to be multiplied by the factor 0.3621 to reduce it to MgO.

Beginners will do well to test the completeness of the separation of magnesia and alumina by examining the solution in which TiO_2 has been determined (p. 114). Alumina and iron are to be precipitated by ammonia in the whole, or an aliquot part, of this, filtered off, and magnesia, if present, determined by the method just described.

6. Ferrous Oxide.

Discussion of the Mitscherlich Method.—The determination of ferrous oxide in rocks has long been a source of difficulty to the analytical chemist and of uncertainty and suspicion to the petrographer. The method which has been most commonly used up to within a comparatively short time, and which is still extensively practised abroad, is that of Mitscherlich, which consists in heating the rock powder with dilute sulphuric acid in a sealed glass tube at 200° till decomposition is effected.

The difficulties of this method are numerous. In the first place, a glass entirely free from iron must be obtained, since the tube is also liable to attack, especially if a little hydrofluoric acid is added, as is sometimes done. The operations for ensuring an oxygen-free atmosphere and the proper sealing of the tube are troublesome, and the heating must be prolonged. Furthermore it is often an extremely difficult matter to ascertain when the decomposition is complete and also, in the case of some iron-bearing minerals, to ensure their complete decomposition under the circumstances.

The fact was noted by Hillebrand * that the determination of ferrous iron by the Mitscherlich method usually gave higher results than that in the same rock, by the alternative method of simple decomposition by boiling with sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide. The explanation was finally found in the observations of Stokes, showing the easy oxidizability of pyrite by ferric salts under the conditions of the sealed-tube method, the iron of the pyrite becoming ferrous sulphate and the ferric sulphate present being partially reduced to the ferrous condition. As, according to Hillebrand, nearly all rocks contain sulphides, and this is especially true of the more basic rocks in which iron is highest, the danger and general inaccuracy of the method are clear.

For most purposes, therefore, and even for the analysis of rocks which are known to be free from sulphur, the Mitscherlich

* Hillebrand, Bull. 176, p. 88; Bull. 305, p. 555.

method is to be discarded, and one of the alternative ones based on the employment of hydrofluoric acid is to be adopted.

Special Grinding of Powder.—Whatever be the method employed for the determination of ferrous oxide, it was formerly thought to be imperative that the rock powder be in an extremely fine state of division, and the use of a specially ground powder was previously advocated by Hillebrand and also by me in the first edition of this book.

A recent investigation by R. Mauzelius* has, however, shown that there is a decided tendency to oxidation of the ferrous iron during grinding, and that this becomes the more marked the finer the powder, so that he recommends the use of as coarse a powder as will be completely attacked by the acid. These conclusions have been confirmed, in the main, by Hillebrand,† who attributes the oxidation to strong local heating at the moment of fracture of the grains under the pestle. The oxidation can be diminished or even completely avoided by grinding under inert liquids, as water, carbon tetrachloride, or alcohol, the last being the most suitable. It must be observed, as regards Hillebrand's investigations, that the times of grinding were very long, at least two hours or more in most cases, a mechanical grinder being used and the powder being reduced to an extreme fineness. When the grinding was half an hour or less the oxidation seems in general to have been negligible.

It follows from these investigations that to obtain correct results for FeO the rock powder must be as coarse as is consistent with proper solution in the acids employed, and that long-continued grinding is to be avoided in preparing the sample. In the method adopted by me for preparing the sample (p. 54), the time spent in crushing is very short and the grinding of the final small residue lasts only 5 minutes or less, so that the oxidation of the resulting powder will be negligible. I have also found that such a powder is easily and completely

* Sver. Geol. Undersökning, Aarbog I, 1907, No. 3.
† Jour. Am. Chem. Soc., XXX, 1908, p. 1120.

attacked and dissolved by the Pratt method in the case of all rocks tested ranging from very acid rhyolites and granites to basic basalts. The main portion of the sample will, therefore, serve for the ferrous oxide determination without further preparation or grinding. For ordinary rock analysis the grinding of the powder under alcohol is not to be recommended, as it involves some sources of error and loss of time through drying.

Simple Method.—There are several modifications of the method of decomposition by a mixture of hydrofluoric and sulphuric acids, which differ in regard to comparative simplicity and, to some extent also, as to accuracy. The simplest, and the one which I have found to be sufficiently accurate for most purposes and by far the most rapid, will be described first. This is essentially the method first tested by Pratt,* and is simpler than that now adopted by the U. S. Geological Survey. I have found it to give accurate and concordant results.

About half a gram of the specially ground rock powder is weighed into a 40-c.c. platinum crucible (p. 144), the cover of which must fit closely. It is moistened with a little water, precautions being taken to avoid blowing out any of the powder. When thoroughly wet and pasty a few small coils of platinum wire are dropped in, to prevent bumping. If carbonates are present in the rock, 1 c.c. of very dilute sulphuric acid is poured in and the cover quickly put on, until effervescence ceases.

In another crucible or small platinum basin a mixture is made of 10 c.c. of hydrofluoric acid and 10 c.c. of a mixture of sulphuric acid diluted with its own volume of cold, boiled water. This warm fluid is poured over the rock powder in the crucible, which is immediately covered and placed loosely in a triangle over a small flame, so that it begins to boil gently almost instantly. The crucible is raised till the boiling is steady, and there is no danger of bumping or boiling over, the proper height for this being learned with a little practice. With a small alcohol lamp and the

* Am. Jour. Sci., XLVIII, 1894, p. 149.

40-c.c. crucible which is regularly used for this operation, I find that about five inches above the flame is the right adjustment. But this will vary with the size of flame and other conditions, so that the analyst must adjust the height according to circumstances.

The boiling is continued for from five to seven minutes, according as the rock is largely feldspathic or rich in ferromagnesian minerals. For the great majority of rocks I have found that six minutes is ample for complete decomposition, and yet not long enough to give rise to sensible oxidation of the ferrous iron by the hot sulphuric acid. There must be no interruption of the regular continuance of the boiling, and the operation should be conducted under the hood or in a place free from draughts.

In the meantime an 800-c.c. beaker is half filled, or at least to a height above that of the crucible, with cold, boiled water, and placed near the crucible with its boiling contents. When the alloted time is up, the still covered crucible is cautiously, but firmly, raised from the triangle (without extinguishing the flame), by means of two flat pieces of wood with a projecting ridge at the ends a trifle wider than the overhang of the cover, and rounded to fit the crucible sides. These are held vertically, one in each hand, and the crucible grasped *near the top*, lifted and dropped into the beaker of water, and the wooden pieces immediately withdrawn.* The contents of the beaker are to be immediately titrated with standard permanganate solution, the burette having been prepared and filled during the process of boiling.

After titration the contents of the beaker should be examined to see if decomposition has been complete, as will be shown by the

* These wooden tongs may be conveniently made of two ordinary test-tube clamps by removing the smaller piece of each, and slightly hollowing the ends to fit the crucible. A long platinum wire with a loop which tightly fits the crucible above the junction with the triangle also serves very well. A pair of Blair's tongs, of German silver, may also be used, if the curved ends are bent so as to lie at right angles with the handles. The operation of transferring the crucible should be first practiced with one half filled with water, till there is no danger of slipping.

absence of hard, gritty particles. With rocks containing much lime or magnesia the liquid will be somewhat turbid, but this need not cause concern as to the decomposition being incomplete. It is due merely to the formation of calcium sulphate and fluorides of calcium and magnesium.

It may sometimes happen, especially with rocks rich in nephelite or minerals which gelatinize with acids, that the powder cakes at the bottom of the crucible, preventing complete decomposition. This is usually due to the powder not having been thoroughly stirred up with enough water before the addition of the mixed acids. In such a case the only remedy is to repeat the whole operation till successful.

The solution of permanganate is to be added till the first blush of red color appears, which is permanent in so far as it does not disappear on stirring. This coloration, however, vanishes very rapidly, more quickly than that produced in the titration for total iron, and as Hillebrand says, the permanganate can be added by the cubic centimeter without obtaining a really permanent color. He attributes* this to the ready oxidizability of manganous sulphate in the presence of hydrofluoric acid.

The influence of hydrofluoric acid in obscuring the end reaction increases with the amount of this acid and with that of manganous sulphate present. Consequently it becomes very serious and renders exact titration very difficult when the rock contains large amounts of FeO, owing to the great quantity of manganous salt formed from the large volume of permanganate solution used. This reaches a maximum in magnetites and other iron ores, such as are produced by differentiation.

To obviate this, R. B. Gage† has proposed a modification, which would appear to be satisfactory and well worth adoption, though I have not yet had the opportunity to test it personally. This consists in rendering the hydrofluoric acid inert by adding

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* Hillebrand, Bull. 176, p. 92; Bull. 305, p. 135.
† Jour. Am. Chem. Soc., XXXI, 1909, p. 381.

calcium phosphate to the liquid prior to the titration, the fluorine precipitating as calcium fluoride. After the crucible has been placed in the beaker of cold, boiled water, ready for immediate titration, about five grams of calcium carbonate converted into phosphate are added and the titration immediately carried out, the first permanent color being taken for the end point. The usually abundant, gelatinous precipitate of calcium fluoride will not interfere with the titration, but if much sulphuric acid is present there may be no precipitation of fluoride. The calcium phosphate is prepared by suspending 5 grams of the calcium carbonate used for the alkali determination in 50 c.c. of water and slowly adding 10 c.c. of 85 per cent orthophosphoric acid while stirring. The beaker should be washed out as soon as possible after titration, to prevent corrosion by the weak hydrofluoric acid.

Pratt's Method.—The simple method described above was modified by Pratt,* by allowing a current of carbon dioxide to flow into the crucible during the boiling by a platinum tube passing through a hole in the cover. As modified by Hillebrand† the method now employed in the Survey Laboratory is as follows. The rock powder in the crucible is mixed with 10 c.c. of dilute sulphuric acid, the crucible is placed in a triangle over the burner, and the air is replaced by carbon dioxide, which enters beneath the lid slightly raised on one side. Before the liquid boils the gas current is stopped and the well-fitting lid is lowered; 5 to 7 c.c. of strong hydrofluoric acid are then quickly poured in through an opening formed by drawing the lid a trifle to one side, the lid is replaced, and the boiling continued for the requisite time. The rest of the operation is as above, and calcium phosphate may also be used if there is very much FeO. This method has certain apparent advantages over the first, but I am inclined to think

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* J. H. Pratt., Am. Jour. Sci. (3), XLVIII, p. 149, 1894.

† Hillebrand, Bull. 305, p. 142.

that there is little to choose between them, so far as accuracy is concerned.

Cooke's Method.—The method devised by J. P. Cooke* was the one employed by the chemists of the Geological Survey,† but is now superseded by the modified Pratt method just described. The methods of Cooke and of Treadwell‡ involve the use of somewhat complicated apparatus, a very lengthy digestion of the rock powder with the acids and a consequent greater risk of oxidation of the ferrous oxide, and often very decided uncertainty as to the complete solution of the rock. They are therefore less satisfactory, and indeed Hillebrand§ points out elsewhere that, in the long series of experiments to study the influence of fine grinding, "there is evidence of a general tendency toward lower results" by Cooke's method than by that of Pratt. For these reasons Cooke's and Treadwell's methods will not be described here, and their use is not to be recommended.

For the influence of sulphides, vanadium and carbonaceous matter on the determination of ferrous iron, the reader may be referred to the discussion of Hillebrand.¶

The percentage of FeO is obtained by multiplying the number of cubic centimeters of permanganate solution used by its equivalent per cubic centimeter in terms of ferrous oxide, and dividing the product by the weight of substance taken. This is then to be calculated as Fe_2O_3 by dividing by 0.9, or by multiplying the number of cubic centimeters by their equivalent in Fe_2O_3 and reducing to percentage amount. The weight of this percentage amount of the portion of the rock powder taken for the fusion with alkali carbonate is calculated, and this weight subtracted from the weight of total iron oxides as Fe_2O_3 as already obtained. The difference, divided by the weight of powder taken for the carbonate fusion, gives the percentage of Fe_2O_3.

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* J. P. Cooke, Am. Jour. Sci. (2), XLIV, p. 347, 1867.
† Hillebrand, Bull. 176, p. 92; Bull. 305, p. 140.
‡ Cf. Hillebrand, Bull. 305, p. 143.
§ Jour. Am. Chem. Soc., XXX, 1908, p. 1131.
¶ Hillebrand, Bull. 176, p. 94; Bull. 305, p. 138.

If an appreciable amount of sulphur as sulphides exists in the rock, regard must be had to the iron in combination with it. If pyrrhotite is the only sulphide present, this will be decomposed by the mixture of acids in the determination of ferrous oxide, and the iron will appear as FeO. The sulphur may be either stated as S in the analysis, or the amount of iron necessary for the molecule Fe_7S_8 of pyrrhotite calculated and deducted from the amount of FeO, and the percentage of pyrrhotite given. The former procedure is rather the better. If the only sulphide is pyrite, this will not be attacked in the determination of FeO, but the iron in this mineral will appear as Fe_2O_3. This may be accorded treatment similar to the iron in pyrrhotite. If both sulphides are present, it will be impossible to estimate the real correction unless the relative amounts of the two minerals are known. Fortunately this is seldom needed, and in general the amount of sulphur is so small that corrections for it are not often necessary.

7. Alkalies.

Alternative Methods.—For the determination of the soda and potash two prominent methods are available. They differ in the means adopted for the decomposition of the rock and for the elimination of all the other constituents, the object of both being to obtain the alkali metals alone in solution as chlorides, and the final separation of these by chloroplatinic acid.

In the older method the rock powder is decomposed by a mixture of sulphuric and hydrofluoric acids, or by fusion with BiO, PbO or B_2O_3, digestion with the acid mixture being that most used. The solution obtained from this is treated successively with ammonia and with ammonium oxalate to remove silica, alumina, iron, titanium, phosphorus and lime. The magnesia is separated by one of several methods (preferably by the use of HgO), the sulphuric acid removed by lead acetate or

barium chloride, and the alkalies determined in the filtrate as in the method described below. Or barium hydrate may be used to separate the other constituents from the alkalies (Classen). It is clear that any of these processes is long and complex, and that, not only do they suffer from the length of time needed, but that there is danger of loss of alkalies during the blasting necessary with some of the fluxes. Still more, the final solution is liable to be contaminated by alkalies derived from the many reagents used and taken up from the glass vessels.

The second method is that of J. Lawrence Smith,* and consists in decomposing the rock by fusion with calcium carbonate and ammonium chloride, leaching with water from the insoluble silicate and aluminate of calcium, and carbonates of iron, calcium and magnesium, precipitation of the rest of the lime by ammonium carbonate, expulsion of ammonium salts by heating the evaporated filtrate, and final separation of the alkalies by chloroplatinic acid.

The advantages of this method are: its convenience and expedition, the manipulations being few, and a day, or at most a day and a half, being ample for the complete determination; the separation of magnesia at the start, which is a troublesome constituent to separate from the alkalies by the other methods; the small danger of introduction of alkalies from reagents or glass vessels, only three reagents being used, and half an hour being the length of time that the hot fluids are in contact with glass; and, finally, its great accuracy, which is fully equal, if not superior, to that of the older methods.† The only real objection which can be urged against this method, as compared with the other, is the difficulty of obtaining a calcium carbonate entirely free from alkalies. The amount of these, however, is easily rendered extremely small by prolonged washing, and it is a con-

* J. L. Smith, Am. Jour. Sci., I, p. 269, 1871.

† Cf. J. L. Smith, loc. cit.; Hillebrand, Bull. 176, p. 96; Bull. 305, p. 333; M. Dittrich, Neues Jahrbuch, 1903, II, p. 81.

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stant error, the correction for which can be safely applied when once determined for the stock of calcium carbonate. Even if this is not done, however, it is certain that the error involved will be less than those incident to the other methods if care be employed in the preparation of the calcium carbonate.

This method is practically the only one which has been used by the chemists of the U. S. Geological Survey, of the extreme accuracy and almost uniquely high character of whose analyses there can be no question. It is likewise the method which I have adopted exclusively, and which is almost universally employed in this country. In Europe, on the other hand, it seems to be little known, or at least little used, and its undoubted merit and superiority over the other are not generally recognized. Only the Lawrence Smith method will be described here.

The Lawrence Smith Method.—For the determination of the alkalies a specially ground portion of rock powder is to be used. Although Smith states that this is not absolutely necessary in all cases, yet it is certainly advisable, as complete decomposition can be secured at a lower temperature and with more certainty than if the powder be coarse.

About one gram of the rock powder is ground down by hand in a small agate mortar, the grinding being continued until a small pinch causes no gritty feeling when rubbed on a tender part of the skin, such as the web connecting the thumb and the index finger or the inside of the wrist. It is then placed in a small special specimen tube, corked and numbered. No appreciable error due to partial oxidation of the FeO is to be feared by this procedure, and it does not involve the great chance of loss of the fine powder incident to the method advocated by Hillebrand* of first weighing out the coarse powder and subsequent grinding.

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* Hillebrand, Bull. 176, p. 97; Bull. 305, p. 145; Jour. Am. Chem. Soc., XXX, 1908, p. 1130.

As the powder is to be mixed with the flux before being placed in the crucible, it is necessary to determine its weight from the loss of substance taken from the tube, instead of by the method of weighing used previously. The small tube containing the specially ground powder is wiped perfectly dry, uncorked, placed on the pan on the small frame intended for this purpose and weighed. The handling of the tube during the operation of weighing is best done by means of wooden tongs, for which an ordinary test-tube holder will answer.

After weighing, and noting the weight as Tube + Subst., a half-gram weight is removed from the right-hand pan, and about half a gram of powder is carefully shaken out into the platinum basin. This must be done with care to avoid any loss of powder, and when a sufficient quantity has been poured in, the tube is to be gently tilted up and lightly tapped to bring the powder down toward the bottom, the mouth being held over the basin. Not more than 0.6 gram need be taken, but not less than 0.45 gram. Half a gram is quite sufficient to yield results fully as accurate as 1 gram, and the consequent saving of chloroplatinic acid solution, as well as shortening of the time needed, are rather important considerations. The tube is then weighed again, and the difference between this weight, recorded as Tube − Subst., and the former gives the weight of substance taken.

Just as in the weighing out of the powder for the alkali carbonate fusion, it may be necessary to shake out and weigh additional small portions several times. The endeavor should be made to get the final weight only slightly above, and as near to 0.5 gram as possible without undue loss of time, and a little practice enables one to do this very quickly. When the powder is in the basin this should be kept covered with a suitable watch-glass to prevent loss by draughts of air.

The balance-pans are then cleared of frame and weights, the pair of balanced watch-glasses substituted, and an amount of dry ammonium chloride equal to that of the rock powder taken is weighed out. It is not necessary that this weight be exact, and it may be a decigram or so more, but should not be less.

This is then poured into the basin with the rock powder and the basin again covered.

An amount of calcium carbonate equal to eight times the weight of rock powder (about 4 grams) is then weighed on the pair of watch-glasses. If a correction for the small amount of alkalies present is to be made this weighing should be carried out to centigrams, but if not, the weighing need be only approximate, but should be more, rather than less, the required amount. With basic rocks 5 grams should be used, to prevent too great fluidity during the fusion.

The weighing out of the rock powder, ammonium chloride and calcium carbonate being finished, the platinum basin and the watch-glass holding the last are placed on a clean sheet of paper on the work-table. A small amount of calcium carbonate is transferred by the platinum spatula to an unweighed 40-c.c. platinum crucible, just sufficient to cover the bottom, and pressed lightly down with the small agate pestle.

The rock powder and the ammonium chloride are then thoroughly rubbed up together in the basin with the agate pestle, after which the greater part of the calcium carbonate is poured into the basin, about half a gram being left on the watch-glass, and thoroughly mixed with the other powder. This is preferably done in small portions at a time, with a rubbing after each addition. The mixture must be thorough, the object being to have, as far as possible, some ammonium chloride and calcium carbonate in contact with each particle of rock, but the rubbing must not be violent.

When the mixing is considered complete, it is well to continue it for a few minutes longer. The pestle is laid down with its lower end in the watch-glass, and the mixture poured cautiously through the lip of the basin into the crucible. This transfer is aided by the platinum spatula in brushing down small lumps at a time, and by final gentle tapping of the spatula on the inside of the basin, so as to cause the whole to pass through the lip without loss outside the crucible. The contents of the crucible are then smoothed down with the spatula, the remaining

calcium carbonate poured into the basin, and the latter rinsed with it by means of the pestle, which is also cleaned at the same time. The spatula is cleaned by rubbing against the carbonate in the basin, and the final portion of this transferred as before into the crucible.

The use of the platinum basin is preferred as a mixing-vessel to that of a large agate mortar, as recommended by Hillebrand, because, while the mixture may be made just as thorough, there is less liability to loss owing to the high sides of the basin, and because the mixed powders are transferred far more easily and safely to the crucible from the basin than from the mortar. I also prefer to have the powder ground specially fine before weighing, instead of after, as recommended by Hillebrand, as the latter is liable to lead to loss.

If the rock is specially ground as fine as has been described, the decomposition will be complete at a temperature not high enough to vaporize the alkali chlorides. An ordinary crucible may therefore be employed, with a well-fitting cover, instead of the capped conical one recommended by Smith and by Hillebrand, which permits a higher temperature for the fusion. The latter is, of course, to be preferred, but it is a somewhat expensive, and otherwise unnecessary, piece of platinum, so that it is as well to know that perfectly satisfactory results may be obtained without its use, if economy be an object.

The crucible is covered and heated over a low flame for ten minutes or so, until no more vapors of ammonia or ammonium chloride are given off. The heating is then continued over the nearly full flame of a Bunsen burner, only the lower third of the crucible being heated to a not very bright red, and the crucible being kept well covered. This is continued for three-quarters of an hour, when the crucible is allowed to cool.

When cold, the mass is soaked in the crucible with just enough water to cover it, and the quicklime formed allowed to slake, by which the disintegration is rendered almost complete. By the aid of the platinum spatula and a little water from the wash-bottle the contents of the crucible are easily transferred to

the platinum basin, any adhering portions being removed by the spatula. A little water is allowed to remain in the crucible to soak it out. The spatula is rinsed off into the basin, which should contain not more than about 50 c.c. of water.

The partially disintegrated mass is well rubbed up with the agate pestle, the pestle rinsed off with a little water, and the contents of the basin brought to a boil, which should be continued gently for a few minutes. The liquid is then decanted through a 9-cm. filter into a 600-c.c. beaker. The stirring-rod is rinsed off into the basin, and the mass once more rubbed up with the pestle till there are no more lumps, the pestle finally rinsed and the basin again heated. The liquid is decanted through the filter, the powder once more heated to boiling with a little water, and finally the contents of the basin brought on the filter. The basin is rinsed, and the contents of the filter washed with hot water, in small portions at a time, the powder being well stirred up by the first additions of water from the wash-bottle.

It is impossible to ascertain when the washing is complete by acidifying drops of the filtrate with nitric acid and testing with silver nitrate, as an oxychloride of calcium is formed which dissolves slowly in water, and will thus give a reaction for chlorine long after all alkalies are washed out. Smith states that complete washing is effected with 200 c.c. of water, but it is as well to be on the safe side and to use 250 to 300 c.c., which will make complete washing certain. This volume may be conveniently marked on the 600-c.c. beaker used for this operation by a small line of paint.

It will be well for the beginner to test the thoroughness of the decomposition by dissolving a portion of the moist mass on the filter in hydrochloric acid. Solution should be complete if the fusion has been properly effected.

To the filtrate a little ammonia water is added and the liquid brought to a boil.* About 1.5 to 2 grams of ammonium car-

* Addition of ammonia is necessary to prevent the formation of soluble calcium bicarbonate. The iridescent scum on the surface of the liquid is, of course, due to the action of atmospheric CO_2 on the calcium hydroxide and chloride.

bonate previously dissolved in 50 c.c. of water* are then added, and the boiling continued for a minute or so. The lime is thus completely precipitated, with the exception of a trace which is separated later, and the alkalies left in solution as chlorides, along with ammonium chloride.

The bulky precipitate of calcium carbonate is allowed to settle a little, and then filtered through a 9-cm. filter into a capacious basin (1000 c.c.). This is preferably of platinum, but as such a large one would be very expensive, a silver basin can be used with equal accuracy. In default of this a glazed porcelain basin will answer, with but slight danger of contamination by alkalies taken up from the glaze, especially as the final evaporation to dryness is carried out in platinum. A glass basin must not be used on any account, as the liquid will be seriously contaminated with alkalies derived from it.

The precipitate is all brought on the filter, the beaker rinsed and the contents of the filter washed with hot water in small portions at a time, till there is no chlorine reaction. The volume of liquid in the basin should be from 400 to 500 c.c. The basin is placed on the water-bath, or on a sand-bath over a flame not high enough to produce boiling, and the liquid evaporated down to about 50 c.c., when it is transferred to the platinum basin, and the larger basin well rinsed with hot water several times. The contents of the platinum basin are evaporated on the water-bath to dryness, which should be complete, as indicated by the white color of the salts. This may be done conveniently by leaving on the water-bath overnight.

The basin, covered with a dry watch-glass, is then placed on a sand-bath and heated gently. This heating must be cautious, and if there is any decrepitation, due to incomplete drying, it should be interrupted frequently till the decrepitation subsides, or otherwise particles of the salts may be thrown up and stick to the cover-glass. If the cover is slightly dewed with moisture at

* The solution of this should be begun when the crucible is put over the flame, so as to have it complete in time. It cannot be hastened by heating, as this decomposes the ammonium carbonate.

first, it is well to remove it frequently and wipe it off quickly, so as to avoid such a mishap. When decrepitation has wholly ceased and white vapors of ammonium chloride begin to rise, the heat is to be raised, with the basin still on the sand-bath. This is continued till the watch-glass and the sides of the basin are thickly coated with ammonium chloride.

The cover is then removed, the basin placed on the ring of a retort-stand and the upper sides warmed with half-full flame to drive off the ammonium chloride. The salts at the bottom are next subjected to the same operation till no more white vapors are given off. Great care must be taken that the bottom of the basin is not overheated so that the salts melt and lead to the possible vaporization of alkali chlorides. During this process the clear white mass becomes dark and dirty-looking, from carbonization of the traces of organic matter which even very pure ammonium carbonate usually contains. Prolonged gentle heating will cause this to disappear to a large extent, but as the carbon is removed by filtration its complete disappearance is not necessary.

After cooling, a little water is added, just enough to dissolve the chlorides. If the rock contains sulphides, and especially if haüyne or noselite are present, a drop of barium-chloride solution is added to precipitate the sulphuric acid, which would otherwise appear later as sodium sulphate and lead to erroneous results. A few drops of the solution of ammonium carbonate are then added to precipitate the excess of barium and the lime which is always present in traces at this stage; or, if no sulphates are present, a few drops of ammonium oxalate solution are added, as this precipitates calcium more completely than the carbonate. After rinsing the interior, as high as the salts extend, by gentle rocking and tipping of the small bulk of liquid, so as to ensure their complete solution, the basin is placed on the water-bath and evaporated again almost to dryness.

Two or three cubic centimeters of water are then poured in to dissolve the salts, and the small amount of liquid filtered through a 5½-cm. filter placed in a small funnel, without suction-tube, into

a previously ignited and weighed 40- or 50-c.c. platinum crucible. The greatest care must be taken in pouring out the first portion of liquid, as drops are apt to fly out of the filter if falling from too great a height. The loss of a single one at this stage would be disastrous, and would necessitate beginning the determination over again from the very start. The basin and filter are washed at least half a dozen times, preferably with warm water, and using only as little as possible, not over 3 or 4 c.c. at a time. When the washing is complete, as shown by a test for chlorine on a single drop toward the last, the crucible should not be more than two-thirds full.

A drop of dilute HCl may be added to the crucible, to decompose any alkali carbonates possibly present, and it is placed on the water-bath, and the liquid evaporated to complete dryness. Care must be taken to ensure this, as small amounts of water caught under the crust resist evaporation for a considerable length of time. It is not advisable, either here or in the evaporation in the basin, to use a platinum spatula or wire to break up the crust and hasten the operation, on account of the danger of loss of substance. The contents of the crucible can usually be rendered dry in three hours or so, if the water be kept at a brisk boil, or it may be left overnight.

When dry, the crucible is placed on a platinum triangle, covered, and very gently heated with a small flame, preferably that of a glass alcohol lamp, held in the hand and moved about at some distance beneath. When the slight decrepitation ceases and vapors of ammonium chloride rise, the flame is gradually raised (but not as far as the crucible bottom), till no more vapors are given off, as may be ascertained by lifting the cover from time to time. The cover is then freed from ammonium chloride by heating over the flame, and the sides of the crucible are similarly treated. The salts at the bottom are then most cautiously heated with the small flame till absolutely no more vapors are given off and they *just* begin to melt in places. When this happens the flame is to be removed instantly. The bottom of the crucible should not be heated above a very faint red, scarcely

visible in daylight. It is to be remembered that one has, on the one hand, to ensure the dryness of the salts and the complete expulsion of ammonium chloride, which would later be precipitated with the potassium chloroplatinate; and on the other, to avoid any vaporization of sodium or potassium chlorides, which, however, only occurs considerably above their melting-points, and need not be feared if this temperature be not exceeded.

If more than a drop or two of ammonium carbonate or oxalate have been used to precipitate the traces of lime, the salts may be darkened by deposited carbon. This will usually be entirely burnt off, or nearly so, in the process of driving off the ammonium chloride and the incipient fusion of the alkali chlorides. The slight amount of it usually remaining is practically unweighable, as my experience has shown, and it may therefore be neglected as a rule.

The platinum crucible containing the salts is cooled in the desiccator, weighed quickly, and the weight recorded as Cruc. + NaCl + KCl. Five or ten c.c. of water are poured in to dissolve the salts, and if the previous operations have been properly conducted the solution will be clear, or at most only a few flakes of carbonaceous matter will be present, which may be neglected as explained above, unless the extreme of accuracy be required. If, however, there is an insoluble residue of calcium carbonate the contents of the crucible must be again filtered, without addition of ammonium carbonate or oxalate, through a small filter into another weighed crucible, the filter washed, again evaporated to dryness, and the operation repeated as before. The crucible and its now perfectly pure contents are weighed, and this weight and that of the new crucible substituted for the former ones. It will be found that the difference seldom amounts to more than a few tenths of a milligram.

Separation of Potash.—To liquid in the crucible a solution of chloroplatinic acid is added to precipitate the potassium as chloroplatinate and thus separate it from the sodium. While it is absolutely necessary to have more than enough of this to

change the entire amount of both sodium and potassium chlorides into chloroplatinates, yet any large excess is to be avoided, on account of the costiless of chloroplatinic acid, if for no other reason. We therefore use a solution of chloroplatinic acid made up to contain 0.1 gram of platinum to the cubic centimeter, as described elsewhere (p. 40). As it will take 1.68 c.c. of this to react completely with 0.1 gram of NaCl to form Na_2PtCl_6, and only 1.31 to do the same with KCl to form K_2PtCl_6, and as nearly all rocks contain both alkalies, we are sure of an excess if we assume that the chlorides are wholly sodium chloride, and calculate the amount of chloroplatinic acid solution used on this basis. We therefore multiply the weight of the combined chlorides by 17, and the result will be the number of cubic centimeters of platinum solution which is to be added. If the rock is extremely rich in sodic minerals, as albite or nephelite, with little or no potash, it will be well to take a few drops more than this.

The crucible is then placed on the water-bath and heated, the water being allowed only to simmer, or attain at most a very gentle boiling, to avoid any dehydration of the sodium chloroplatinate, although I have never observed this to happen, even with a fairly brisk boiling. If the precipitated potassium chloroplatinate does not wholly dissolve when the liquid has become warm, a few cubic centimeters of water are to be added to permit its solution. This will seldom if ever be necessary if the directions and strengths of solutions given above are followed, even with highly potassic, leucite rocks.

The contents of the crucible are evaporated, with occasional slight shaking, to break up the crust as it forms, till the liquid mass solidifies on cooling. This will take place when the depth of the liquid is reduced to about 2 mm., but is naturally dependent on the amount of alkalies in the rock. The evaporation should never, under any circumstances, be carried to complete dryness on the water-bath, as partial dehydration of the sodium salt will occur, the anhydrous sodium chloroplatinate being soluble with some difficulty in alcohol, and thus possibly adding to the apparent amount of potassium.

When the evaporation is finished the crucible is removed, covered, and allowed to cool, so as to make sure that the liquid solidifies. It is then half filled with alcohol of 0.86 specific gravity,* contained in a small wash-bottle, and allowed to soak. In the mean time the Gooch crucible is prepared with an asbestos felt, as already described (p. 132), ignited, cooled and weighed, and placed in position above the Erlenmeyer flask.†

By this time the disintegration of the solid mass in the crucible should be complete. If not, it may be hastened by stirring and rubbing cautiously with the lower end of a 5-c.c. pipette, the lower aperture of which should be from 1 to 2 mm. wide. When solution is complete, except for the precipitated, golden-yellow crystals of potassium platinichloride,‡ the suction is started beneath the Gooch crucible and the fluid is transferred to it by means of the pipette. For this purpose the crucible with the liquid is held in the left hand close to the Gooch, a little liquid sucked up into the pipette and allowed to run down the sides of the filter, to avoid breaking the felt. When all the liquid has been thus decanted, a little more alcohol is poured on the precipitate in the crucible, and decanted as before into the Gooch when this is empty. After three or four decantations, by which time the soluble salts are nearly gone and the liquid almost colorless, the sides of the Gooch crucible are carefully washed down with a stream of alcohol, and the pipette rinsed both inside and out into the Gooch, which is more than half filled with alcohol

* If a hydrometer is not at hand an alcohol of approximately this specific gravity may be made by mixing five volumes of ordinary 95 per cent alcohol with one volume of water. Mauzelius (Bull. Acad. Sci. Crac., 1906, p. 796), has shown that, when Na_2PtCl_6 is present, alcohol stronger than 80 per cent decomposes the sodium salt, precipitating sodium chloride. An alcohol of less strength than 75 per cent dissolves appreciable amounts of K_2PtCl_6 (cf. Jour. Am. Chem. Soc., XXX, 1899, p. 755).

† If this has been previously used for the determination of magnesia, it, as well as the carbon filter and rubber, must be thoroughly washed free from all traces of ammonia.

‡ If the fluid is not yellow, or if small white grains (of sodium chloride) are present among the yellow crystals of K_2PtCl_6, there has not been enough platinum solution added. About 2 c.c. and a little water are to be added and the liquid again evaporated nearly to dryness.

to protect the felt. The bulk of the precipitate is then transferred to the filter, without the use of a rod, by a gentle stream from the alcohol wash-bottle, the depth of liquid above the felt being so great that the drops can fall in the center without danger.

With a slender stirring-rod capped with a bit of fine rubber tubing the small quantity of adhering potassium chloroplatinate is loosened and is washed into the filter, the stirring-rod being also rinsed off. Owing to the bright color and the high specific gravity of the precipitate, it is easy to be sure of its complete transfer. When the Gooch is again empty it is well washed, at least half a dozen times, the sides being also washed down, inside and out. Enough alcohol may be added each time to half fill the crucible, but it must be allowed to empty before another addition. After washing for the last time, aspiration is continued for a few minutes to partially dry the felt.

The final drying is accomplished in an air-bath at a temperature of 135°, which is necessary to drive off all the water. The bottom cap of the Gooch crucible is placed in position, and the crucible covered while in the air-bath with a 7-cm. filter-paper instead of the cover. This facilitates evaporation, and at the same time guards against particles falling in from the top of the air-bath. The drying will usually be complete in half an hour, but it is as well after heating for this time and weighing, to reheat for another fifteen minutes, or to constant weight. After cooling in the desiccator the Gooch crucible is weighed, and recorded as Gooch + K_2PtCl_6. The weight of the potassium chloroplatinate is multiplied by 0.1940 to arrive at the weight of K_2O, from which is to be subtracted the amount of K_2O present in 4 grams of the calcium carbonate used, if this has been determined.

The weight of K_2PtCl_6 is then multiplied by 0.307 to reduce it to KCl, and the weight of this deducted from that of the mixed chlorides. The weight of the NaCl thus obtained is multiplied by 0.5308 to reduce it to Na_2O, which is to be corrected for the amount of Na_2O present in the calcium carbonate.

If a Gooch crucible is not available the method followed by Hillebrand may be adopted. This consists in filtering off the excess of chloroplatinic acid solution through a small filter (5½ cm.) and washing with alcohol, as little of the precipitate as possible being brought on the filter. When the precipitate has been washed free from all soluble matter the small amount on the filter is washed into the weighed crucible by small amounts of hot water, the excess of liquid evaporated to dryness on the water-bath, and the precipitate finally dried as above at 135°. Hillebrand prefers the use of porcelain for the evaporation of the alcoholic platinum solution, but for most work this is hardly necessary.

It is seen that the amount of Na_2O is determined by difference. But, in view of the accuracy of the method, this is preferable to a direct determination in the filtrate. If it is desired to do this, the filtrate is to be freed from platinum by one of the methods recommended by Hillebrand, and the sodium determined as sulphate in the usual way, by evaporation with sulphuric acid.

As Hillebrand says, there is scarcely ever enough lithium present in igneous rocks to warrant its quantitative estimation. It is almost invariably present in spectroscopic traces, but, so far, there seems to be little theoretical necessity of establishing this fact in every rock analysis. If it is desired to do this, the filtrate is to be evaporated to dryness and tested with the spectroscope. If it be desired to estimate it quantitatively, Hillebrand's directions and his summary of Gooch's method are to be followed.*

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* Bull. 176, p. 99; Bull. 305, p. 148.

8. Combined Water.

Under this head is included all the water in a rock which is chemically combined in mineral molecules, either as water of crystallization (as in analcite) or hydroxyl (as in muscovite or biotite).

Loss on Ignition.—The early method, and a very frequent one even at the present day, for the determination of this constituent, was that of simple ignition in a platinum crucible, the assumption being that this "loss on ignition" represents only the total water in the rock. A little consideration shows that the results under these circumstances will only be accurate when the rock contains neither substances which are easily volatilizable at the temperature of ignition (as carbon dioxide, carbon and organic matter, sulphur, chlorine and fluorine) nor oxidizable constituents (as ferrous oxide). In the former case the apparent amount of water will be too great, owing to the partial or entire loss of the volatilizable ingredients, and in the latter it will be too small, on account of the gain in weight through the oxidation of ferrous oxide to ferric.*

It is held by some that the error due to the latter cause may be corrected by calculation of the gain in weight which the ferrous oxide present in the rock, and which is separately determined, would undergo if completely oxidized to ferric oxide. This assumption, however, is by no means valid under the circumstances obtaining in the process of ignition, as is shown, for example, by the difficulty of completely oxidizing magnetite by ordinary ignition, even after roasting with nitric acid.

In the case of volatilizable constituents, also, there can scarcely ever be a certainty that their loss in this way will be complete, so that appropriate corrections may be made with

* This may be so great that if little water and much ferrous oxide are present, the powder may weigh more after ignition than before.

safety after their separate determination. This would only be true of carbon dioxide when derived from calcite, magnesite or dolomite, and then only after prolonged blasting.

This being so, and it being also a fact that there are only rare instances of rocks which contain no such disturbing constituents (especially FeO), it follows that in the great majority of cases the combined water should not be determined by loss on ignition.

As, however, the determination of combined water is not always of vital importance for the chemical study of rocks, it happens that this simple method may be used in certain cases. These would include very fresh igneous rocks, containing but a small amount of water, no other volatilizable ingredients, and only a small amount of ferromagnesian minerals, say up to 5 per cent, and consequently only 1 or 2 per cent of ferrous iron. Many granites, porphyries, syenites, trachytes, rhyolites, and anorthosites fall under this description. For such rocks the minute error due to the very small amount of ferrous oxide present (amounting at most to one-ninth of its weight) may be deemed to be negligible, and the results of such a determination regarded as acceptable.

If the method of "loss on ignition" is to be employed, the crucible and its contents, which have previously been used for the determination of hygroscopic water, are ignited (covered) at a bright-red heat for about half an hour, or to constant weight, cooled in the desiccator and weighed. The loss in weight represents the amount of combined water. The fact must, however, be recognized that this method of procedure is not strictly accurate, and for all high-class work, and in all cases where the amount of ferrous oxide is at all considerable, or volatilizable substances are present, the combined water must be determined directly.

Penfield's Method.—For the direct determination of water the extremely easy and simple method of Penfield is to be used.* This consists essentially in igniting the rock powder in a narrow

* S. L. Penfield, Am. Jour. Sci., XLVIII, p. 30, 1894.

tube of hard glass, closed at one end and with or without enlargements in the middle, pulling off the heated end containing the powder and leaving the balance of the tube closed, weighing the portion of the tube which contains the expelled water, and finally weighing this portion of the tube after thorough drying. This gives the total amount of water, hygroscopic and combined, from which the amount of the former, as previously obtained, is to be deducted to obtain the latter. For illustrations of the apparatus used the reader is referred to the paper cited above.

In the case of most fresh igneous rocks a simple tube of hard glass may be used, closed at one end, and without any enlargement. The dimensions recommended by Penfield are 20 to 25 cm. long,* and with an internal diameter of about 6 mm. If the rock contains more than a fraction of a per cent of water it is better to have a bulb or enlargement blown about midway in the tube. Indeed, this is always advisable, to guard against drops of water rolling back on the heated portion. A single bulb is sufficient for nearly all rocks, and the more complicated forms illustrated by Penfield will seldom be found necessary in rock analysis, unless the rock is not fresh.

It is of the utmost importance to have the tube thoroughly dry, and this "is best accomplished by heating and aspirating a current of air through it (while hot) by means of a glass tube reaching to the bottom." This must always be done, even if the tube is apparently dry. After cooling, the tube is weighed, its weight including that of the brass-tube support which is used to support it on the balance-pan.

From one-half to one gram of the rock powder is then introduced, filling the tube about 2 or 3 cm. from the closed end. This must be done without soiling the upper portion of the tube, and is accomplished by means of a small thistle-tube, of diameter small enough to slip easily into the bulbed tube, and long enough

* The tube must not be too long to go in the balance-case, and so interfere with weighing, nor too short, so as to give rise to the danger of loss of water through lack of sufficient cooling surface and heating of the cooler portion.

to reach the end. Such a filling-tube can be readily constructed from a 5-c.c. pipette by cracking the bulb in two and reducing the length of the tube to 25 cm. The filling-tube, of course, must be thoroughly dry also.* After the powder is introduced the tube is weighed again, to obtain the weight of substance used, the manipulation being delicate and gentle to avoid any rolling of the powder toward the open end.

After a few gentle taps so as to form a free passage above the powder for the heated air, which might otherwise drive the powder toward the bulb and so necessitate refilling and reweighing, the tube is held in a clamp horizontally, or *very slightly* sloping toward the mouth. A strip of filter-paper or cloth, moistened with cold water and kept moist, is wrapped around the bulb and farther end of the tube, so as to ensure condensation of the expelled water, care being taken that it is not so near the mouth as to allow any water dropped on it to enter the tube.

A gentle heat is then applied to the closed end, and gradually increased to the full heat of the Bunsen burner. The blast may be used if minerals are known to be present which only give off their water with difficulty, but this will not be needed in most rocks. If the strip of cloth or filter-paper be kept moist, there is scarcely need for a screen of asbestos board, nor is it often necessary to partially close the tube with another short piece of tube drawn out to a capillary and connected by rubber tubing. If the heated end of the tube tends to sink, this should be prevented by gently turning it round from time to time parallel to its axis, the clamp being adjusted so as to allow of this being done.

After the whole extent of the powder has been ignited and the water completely expelled, which will take at least a quarter of an hour, a short piece of narrow tubing is melted onto the closed tip, to serve as a handle. The flame is then lowered and the water

* The thistle-tube can be easily cleaned "by drawing through it a bit of cotton attached to a wire," or, if the analyst be a smoker, a fresh pipe-cleaner will be found useful.

is very gently and gradually driven into the bulb. This must be carried out with caution and patience to avoid cracking the tube. When the water has been driven into the bulb and to a safe distance, the portion of the tube immediately in front of the powder is heated to softness all around, and the end containing the powder drawn off and the other part sealed without allowing the flame to enter. This last procedure is not strictly necessary in all cases, but is always advisable, so as to obviate the possibility of loss of powder during the subsequent drying and aspiration.

The upper portion of the tube containing the water is allowed to cool in the clamp in a horizontal position, wiped clean and dry on the outside and weighed. It is well to test the water with blue and red litmus-paper. It is then placed again in the clamp and gently heated, the moist air and steam being sucked by out means of a small tube extending to the bottom and connected with a suction-pump. After thorough drying in this way it is allowed to cool and is again weighed.

The loss in weight is the amount of total water, which is reduced to percentage figures by division by the amount of substance taken, and the percentage of hygroscopic water already determined is subtracted.

In nearly all cases the simple method described above will be quite sufficient and will yield very accurate results. But when rocks, such as some metamorphic ones, contain minerals like topaz, chondrodite, or staurolite, whose water is not completely driven off over the blast, it becomes necessary to use a more intense method of heating. For a description of this, reference may be made to Penfield's article.

If the rock contains constituents like SO_3, S, Cl or F in appreciable amount, which are volatile and which will add to the weight of the water driven off and condensed, it is necessary to use a retainer for these during the ignition. This may be best CaO, previously ignited to constant weight and cooled.* A

* Penfield and Howe (Am. Jour. Sci., XLVII, 1894, p. 191) state that lead oxide, which is often used, is wholly unsuitable.

little of this is introduced by means of the thistle-tube into the bulbed tube, after the rock powder has been weighed, and mixed " by means of a fine wire, bent into a corkscrew coil at the end." A decigram or two will be ample for most rocks. In ordinary rock analysis the correction for CO_2, described by Penfield, will not be necessary.

With the usual run of rock analyses the more complicated apparatus of Penfield or Gooch, involving the use of absorption-tubes, will seldom be called for. For a description of them the references below had best be consulted if their use be deemed desirable.*

9. Hygroscopic Water.

By this term is meant the moisture which is adsorbed by the rock powder from the atmosphere, or which may come from that enclosed in microscopic cavities, although a part of the more loosely combined water of crystallization of some zeolites and other hydrous minerals may also be included under this head. It is all, or practically all, expelled from the rock at a temperature of about 110°. Although it is usually present only in very small amount, and has no important bearing on the constitution of fresh igneous rocks, yet it should always be determined separately from the combined water. The reasons for this have been fully discussed by Hillebrand † and need not be gone into here.

The influence of the fineness of the powder on the adsorption of moisture from the atmosphere, and the consequent advisability of analyzing air-dry material, has already been mentioned (p. 58).

About 1 gram of the rock powder is weighed out into a previously ignited and cooled platinum crucible of 30 or 40 cc.

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* S. L. Penfield, Am. Jour. Sci., XLVIII, p. 37, 1894; F. A. Gooch, Am. Chem. Jour., II, p. 247, 1880; Hillebrand, Bull. 176, pp. 40–47; Bull. 305, pp. 62–68.

† Hillebrand, Bull. 176, p. 32; Bull. 305, p. 53.

capacity (cf. p. 80), and this is heated in an air-bath at a temperature a little above that of boiling water. The exact temperature is of no great importance, as long as it is only slightly above 100°. In the U. S. Geological Survey laboratory a toluene bath is used, giving a temperature of 105° (Hillebrand), while my practice has been to use an ordinary copper air-bath, with single walls, and the flame so regulated as to maintain the temperature constantly at 110°, which is readily accomplished. The crucible is preferably covered during the heating with a 7-cm. filter-paper, the platinum cover being removed. It will usually be found that half an hour's heating, and often less, will be sufficient to arrive at a constant weight. After heating, the crucible is allowed to cool in a desiccator and weighed, heated again for a quarter of an hour, and if the weight is constant, the loss in weight, divided by the weight of rock powder taken, gives the percentage of hygroscopic water, which may be conveniently tabulated as H_2O—.

10. Phosphoric Anhydride.

As the amount of material is usually ample in rock analysis, it is the best plan to determine this constituent in a separate portion of rock powder, although it can also be determined in the solution used for the total iron and titanium dioxide, as mentioned below.

On the ground that simple digestion with nitric acid does not ensure complete solution of phosphoric anhydride in all cases,* Hillebrand† recommended the fusion of the rock powder with alkali carbonates and subsequent treatment to separate silica, as before described (p. 81), except that HNO_3 is used in place of HCl, and a single evaporation is sufficient. The silica is to be

* This would be largely because apatite occurs in the form of microscopic needles, which often form inclusions in minerals unattacked by nitric acid. Therefore if the rock powder contains grains of such minerals with unexposed inclusions of apatite, these will not go into solution.

† Hillebrand, Bull. 176, p. 78.

evaporated to dryness with hydrofluoric and a few drops of sulphuric acids, the residue dissolved in a little boiling nitric acid and added to the main filtrate from the silica. This is evaporated to small volume, and the phosphorus precipitated with ammonium molybdate, after the addition of some ammonium nitrate.

While this process will undoubtedly yield the whole of the P_2O_5, it is somewhat lengthy and complex. Simple digestion with a hot mixture of nitric and hydrofluoric acids decomposes the rock powder completely, and furnishes equally satisfactory results, at the same time being far more expeditious. The use of the following simple method* is therefore advocated, and it is now adopted in the Survey Laboratory.†

About 1 gram of rock powder is weighed out into a small platinum basin, or if that is not available, into a capacious crucible. The rock powder is then mixed with 10 c.c. of water, taking the precautions to prevent loss noted previously, and stirred up with a small platinum spatula or platinum wire which is left in the basin for stirring. Ten c.c. of concentrated nitric acid are added, about 5 c.c. of hydrofluoric acid are next poured in, and the mixture is evaporated to dryness on the water-bath or over a low flame with occasional stirring. This is to render insoluble any silica which might otherwise come down with the phosphorus. Evaporation with small quantities of nitric acid alone is to be repeated two or three times, to decompose the fluorides.

When completely dry after the last evaporation, the basin is heated till its contents become brown, and when cool the crust is moistened with 5 c.c. of a mixture of nitric acid diluted with twice its bulk of water, and gently boiled for a few minutes, which will convert any meta- or pyro-phosphates, possibly

* This is the method described in the first edition, as modified by Dr. Hillebrand and me independently, the first filtration before the evaporation being omitted.

† Hillebrand, Bull. 305, p. 121.

produced by the heating, into orthophosphates.* Solution will be complete, except for the silica and fluorides present, and the liquid is filtered through a 5½-cm. filter into a 100-c.c. beaker. The beaker is to be rinsed out and the filter washed half a dozen times with the same warm dilute acid, less than 50 c.c. in all sufficing for this. Twenty-five c.c. of ammonium molybdate solution are to be added, or 50 c.c. if the rock contains much P_2O_5. The liquid is stirred, and laid aside (covered) for at least twenty-four hours in a warm place.

The liquid is then filtered through another 5½-cm. filter, the bright-yellow precipitate being disturbed as little as possible. The latter is washed with a mixture of weak solution of ammonium nitrate, nitric acid and ammonium molybdate solution in equal parts, till the addition of ammonia water in excess produces no permanent precipitate in a few drops of the filtrate in a watch-glass. About 50 c.c. of the washing mixture will usually be ample, and it can best be prepared in a small beaker as needed.

The phosphorus is now all in the precipitate of ammonium phosphomolybdate, and the beaker containing the greater part of this is placed beneath the funnel, which is then filled with ammonia water diluted with an equal amount of water. This dissolves the small portion of precipitate in the filter and part or the whole of that in the beaker, assisted by stirring. If solution is not complete some more ammonia must be added. The filter is then well washed, half a dozen fillings with water being sufficient.

If the fluid in the beaker is turbid, due to the formation of a white compound of phosphorus, as occasionally happens, this may be overcome by the addition of a small fragment of citric or tartaric acid. If this fails to remove the turbidity, the liquid is to be filtered through the same filter into another small beaker, the filter ignited in a small platinum crucible and fused with a pinch of sodium carbonate, the small cake dissolved in water, acidified with nitric acid, and the solution added to the rest

* Cf. Treadwell, I, pp. 322, 323.

(Hillebrand). This has never been necessary in my experience.

To the solution in the beaker, which may amount to 50 to 100 c.c., 10 c.c. of magnesia mixture are added, best through the same filter, to remove any possible deposit in the magnesia mixture. The beaker is allowed to stand for twelve hours, then filtered through a small filter and the precipitate collected on the latter, that adhering to the sides of the beaker being rubbed off, the filter and precipitate of ammonium-magnesium phosphate well washed with weak ammonia water.

The filter with its contents are then placed in a small weighed platinum crucible, and, after the filter has been carbonized, ignited at a bright-red heat. When cool it is weighed, and the weight of the $Mg_2P_2O_7$ multiplied by 0.638 to reduce it to P_2O_5. The appropriate weight of P_2O_5 determined from this percentage is to be deducted from the weight of the precipitate by ammonia water (p. 106), to arrive at the correct weight of alumina.

It may be borne in mind that, as the phosphomolybdate precipitate contains only about 3.5 per cent of P_2O_5, if there is only a minute quantity of it, the phosphoric anhydride present will be so small in amount that it need not be determined, but may be stated as a "trace." It is best, however, in all cases to carry the operation through to completion, especially when one has had no experience as to what is a sufficiently small amount of precipitate to justify neglect of the succeeding operations.

The above is the usual procedure, but much time may be saved, with no sacrifice of accuracy, by adopting Woy's method of precipitation and determination as phosphomolybdic anhydride.* This, somewhat modified, is the method which I now generally use. For this are required the usual solution of ammonium molybdate, a solution of 340 grams of ammonium nitrate in 1 liter of water, and a wash liquid made up of 50 grams of ammonium nitrate and 40 c.c. of nitric acid in 1 liter of water.

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* Treadwell, II, p. 346.

The solution of the rock obtained as above and amounting to about 50 c.c., is held in a 250-c.c. beaker, about 25 c.c. of the ammonium nitrate solution are added, and the liquid is gently heated until bubbles begin to rise. In the meantime about 25 c.c.* of ammonium molybdate solution are heated to boiling in a small beaker, and then poured in a thin stream into the hot rock solution, which is kept in rotation by a stirring rod. Precipitation is immediate and complete. The liquid is rotated a few minutes more, allowed to stand 15 to 20 minutes, and the clear liquid poured off through a small filter. It is best to redissolve the precipitate in dilute ammonia water and reprecipitate, which is done exactly as before.

To determine the P_2O_5 as phosphomolybdic anhydride, the yellow precipitate is collected in a weighed Gooch crucible and washed with the wash liquid mentioned above, about 50 c.c. being usually ample. The lower cap is then put on, and the crucible is gently heated until the contents are dry and no more vapors of ammonia or ammonium salts arise. The heat is then raised until the bottom is a dull red and this is continued until the yellow mass is entirely decomposed into the greenish-black anhydride, $24MoO_3.P_2O_5$. About ten minutes suffices for this. The weight of the anhydride multiplied by .0395, or by .04 for the usual small amounts, gives the weight of P_3O_5. According to my experience the method is rapid, accurate, and satisfactory.

Of course, if preferred, the yellow precipitate obtained as above can be redissolved in dilute ammonia water, and the phosphorus precipitated with magnesia mixture and weighed as $Mg_2P_2O_7$, in the usual way.

If material be scanty and it is desired to determine phosphoric anhydride in the solution used for total iron and for titanium dioxide, the following process will serve: The acid solution, or an aliquot portion of it, after determination of TiO_2, is precipitated with ammonia, the precipitate washed with hot

* If the rock contains more than 1 per cent of P_2O_5 50 c.c. must be used.

water a few times, dissolved on the filter with dilute nitric acid and the filter washed, the filtrate and washings evaporated to small bulk, and the phosphorus precipitated in this by ammonium molybdate. The subsequent operations are as described above.

11. MANGANESE.

Walter's Colorimetric Method.*—The gravimetric determination of manganese in the main portion used for silica, etc., has been already described (p. 124). For reasons previously mentioned it will be usually found advisable not to follow this procedure, but to determine the manganese in a separate portion, for which purpose the following method is admirably adapted, being simple, rapid and highly accurate for the smal quantities of manganese commonly present.

A standard solution of manganese, containing 2 mg. of MnO in 10 c.c., is needed. This is prepared best by dissolving 0.4455 grams of the purest potassium permanganate in 500 c.c. of water (held in a 1000-c.c. measuring-flask with stopper), for which at least 24 hours should be allowed. To this 5 c.c. of sulphuric acid are added, and then the permanganate reduced by the very cautious addition of solution of sulphur dioxide until the liquid just becomes colorless, when it is diluted to 1000 c.c. and well shaken. A solution containing 2, or better 3, grams of silver nitrate per liter is also necessary.

About 1 gram of the rock powder is weighed out into a capacious platinum crucible, or better a small platinum basin, and 10 c.c. of sulphuric acid (1:1) and 5 c.c. of hydrofluoric acid are poured in. After thorough mixing with a small platinum spatula or wire, the mixture is heated gently until the powder is wholly decomposed, and then more strongly until white fumes of SO_3 are given off. After cooling another 10 c.c. of sulphuric acid are added and the heating repeated, this being done two or three times more to ensure the expulsion of the

* H. E. Walters, Chem. News, LXXXIV, 1901, p. 239. The description here given is based on that of Hillebrand, Bull. 305, p. 99.

hydrofluoric acid. The last time it is best to heat almost to dryness. About 10 c.c. of nitric acid, which should be free from chlorine, and the same amount of water are added, and the mixture gently heated for 10 minutes or so to dissolve all possible. The insoluble residue, chiefly calcium and possibly barium sulphates, is filtered off through a small filter and washed with small portions of hot water, the filtrate and washings being caught in a 100 c.c. beaker. They should not amount to more than about 50 c.c.

To the clear rock solution 10 c.c. of the silver nitrate solution are added for each milligram, or 0.10 per cent, of manganese present in the rock. For very silicious rocks, as granites or rhyolites, 10 c.c. will be ample, but for more basic rocks 20 or 30 c.c. should be used. It is essential to have an excess of silver nitrate, and I therefore prefer a solution of 3, rather than 2, grams to the liter. If there is a precipitate of silver chloride, as will happen if the rock contains sodalite or scapolite, the liquid is to be well stirred to coagulate the precipitate and filtered into another small beaker, the filter being washed twice with a little water.

About 1 gram of solid ammonium persulphate is added and the beaker gently heated over a low flame. The salt dissolves with a crackling noise, and as the liquid warms the pink color of the permanganate appears, which gradually deepens until it attains a maximum. Soon after the color begins to appear, it is best to remove the beaker from the flame and place it in a basin containing some cool water until the color has reached its greatest depth. With some rocks, or under certain conditions which are not clearly known, the color of the liquid is a peculiar red, due probably to the presence of manganic salts, rather than the true purplish-red of permanganates. In this case the liquid must be allowed to stand, possibly for 24 hours or more, until the normal color appears, as otherwise exact comparison with the standard cannot be made. The solution is now poured into a 100-c.c. measuring-flask, with stopper, unless the rock contains much manganese, when a 200- or

250-c.c. flask is to be used. The solution will retain its full color unchanged for several days, the rapidity of the change being the less the stronger the solution, so that one should not dilute up to the mark until one is ready for the comparison, if a series of manganese determinations are to be carried out.

In another 100-c.c. measuring-flask there are placed by means of a 10-c.c. pipette 10, 20, or 30 c.c. of the standard manganese solution, the amount depending on the depth of color of the test solution. The color of the standard, when oxidized to permanganate, must be considerably deeper than that of the test solution. Ten c.c. is usually enough. The required amount of silver nitrate solution, 20 c.c. for each 10 c.c. of manganese solution, is added, then 1 gram of solid ammonium persulphate, and the solution is oxidized exactly as above. When cool it is diluted to the mark, thoroughly mixed, and poured into a burette. Ten c.c. are drawn off into one of the rectangular glasses used in the titanium determination (p. 116), the other containing some or all of the test solution, and the standard diluted with water from another burette until the colors match, the whole process being carried out exactly as was done with titanium. The calculation of the amount of manganese is exactly analogous to that of titanium, due regard being paid to the amount of standard manganese solution used. If ammonium persulphate has been added prior to the precipitation of the main portion by ammonia, the weight of the manganese, calculated as Mn_3O_4 by multiplying the weight of MnO by 1.075, is to be subtracted from that of the ignited ammonia precipitate of alumina, etc.

If there is a deficiency of silver nitrate a brown precipitate of hydrated manganese oxide will form on heating after the addition of the persulphate. If this happens with the test solution, a little SO_2 water is added to dissolve the precipitate, another 10 c.c. or so of silver nitrate added, and the solution reoxidized as before with the addition of a little more persulphate. In the case of the standard solution, it is best to begin again with a fresh portion, adding more silver solution than before.

12. Total Sulphur, Zirconia and Baryta.

These constituents may be determined in separate portions, but it will be found to be a great economy of time to determine them in the same portion by the following plan, which was first published by Hillebrand,* and independently worked out by myself. The whole process, while apparently complicated, in reality takes very little extra time for its execution, as the volumes of liquid are small, and the various operations may be carried out during pauses between the main determinations, when solutions are being evaporated, etc.

Decomposition.—For this set of determinations 1 gram of rock powder is sufficient. About this amount is weighed out into a weighed platinum crucible, mixed with four or five times its weight of mixed sodium and potassium carbonates, and fused precisely as has been described above (p. 81).

If pyrite is present, and it is desired to determine the sulphur, a small quantity, about one-quarter of a gram, of powdered potassium nitrate is mixed with the carbonates, which should have been tested to see if they are free from sulphur or sulphates. If much nitre is used the crucible is liable to be attacked. The reaction between the nitrate and the carbonates gives rise to considerable effervescence, and the fusion should therefore be carried on cautiously, and at as low a temperature as possible, till all nitrous fumes have disappeared. The temperature may then be raised and the operation carried on as above.

When the cake is perfectly cold it is detached from the crucible and thoroughly leached with water, till all soluble matter is dissolved, a drop or two of alcohol being added to reduce any sodium manganate which may be present.

Of the constituents which immediately concern us, the sulphur (that as sulphide as well as that as sulphate) passes into solution as sodium sulphate, while the BaO and ZrO_2 remain un-

* Hillebrand, Bull. 176, p. 73.

dissolved, the former as barium carbonate and the latter as sodium zirconate.

Sulphur.—The liquid is filtered through a 7-cm. filter, as little as possible of the undissolved residue being brought on this, and the residue and filter are well washed with a very dilute solution of sodium carbonate to prevent turbid washings (Hillebrand). The further treatment of the residue will be found below under Zirconia.

If the filtrate shows a yellow color the presence of chromium is indicated, and this element is to be estimated in a separate portion, as described on p. 165. In general, however, it is absent, and in any case we can proceed at once to the determination of the sulphur, as the free hydrochloric acid present prevents the precipitation of barium chromate.

The filtrate, which should amount to from 150 to 250 c.c. in a 400-c.c. beaker, is colored with two or three drops of methyl-orange solution, and hydrochloric acid is added gradually through a small funnel with curved tip, the beaker being covered to prevent loss, till the original orange color changes to pink, indicating that the liquid is acid. About half or, at most, 1 gram of barium chloride dissolved in 25 c.c. of water is added to the boiling liquid, the cover and sides washed down, and the beaker allowed to stand till the barium sulphate has settled. There is little danger of silica contaminating the barium sulphate, in the bulk of liquid recommended above, but if this should happen it is removed later. It is obvious that failure of barium chloride to produce a precipitate indicates the absence not only of S, but of SO_3. In this case this last need not be looked for, but both may be stated in the tabulation as absent.

The liquid is filtered, all the barium sulphate being brought on a small filter (7 cm.) by means of a rubber-tipped rod and the wash-bottle, and the filter well washed. The filter is ignited in a small weighed crucible, the barium sulphate evaporated with a few drops of hydrofluoric and one of sulphuric acids to expel any silica possibly present, again ignited and weighed. Further purification of the barium sulphate is seldom necessary.

If no SO_3 is present in the rock, the weight of $BaSO_4$ is multiplied by 0.137 to reduce it to S. If SO_3 is present, the weight of $BaSO_4$ is multiplied by 0.343 to reduce it to SO_3, which is changed to percentage figures by division by the weight of substance taken. From this the percentage of SO_3 present in the rock as obtained in a separate portion (p. 174) is deducted, and the remainder multiplied by 0.401 to reduce the SO_3 to S.

Zirconia.—The whole of this is present as sodium zirconate in the residue insoluble in water. The small part of this which adheres to the filter is washed back into the beaker containing the bulk of the residue, by holding the funnel sidewise and directing a strong stream of water from the wash-bottle against all parts of the filter, the liquid dropping into the beaker beneath. With care, and if done while the residue is still moist, the removal can easily be made complete.

To the contents of the beaker, the bulk of which should be less than 50 c.c., not more than three or four drops of concentrated sulphuric acid are added. A larger amount is to be avoided, as too much free sulphuric acid prevents the entire precipitation of the zirconia (Hillebrand), and also retards filtration through action on the filter-paper. The liquid is warmed (not boiled) till all effervescence ceases, and another drop of sulphuric acid added to see if solution has been complete. The liquid should be distinctly acid. If so, the liquid is filtered through the original filter into a flask of about 100 c.c., and the filter and beaker are washed several times with small quantities of warm water.

The filtrate now contains all the zirconia as sulphate, while the baryta remains behind as insoluble barium sulphate, along with strontia and some lime and silica. For the treatment of this insoluble portion, see p. 173.

To the filtrate in the flask is now added about 5 c.c. of hydrogen peroxide, or enough to cause a permanent yellow coloration, and then a few drops of a solution of a soluble phosphate, as microcosmic salt. The flask is filled nearly to the neck, if not so already, and set aside in a cool place for at least twenty-four hours, and preferably for twice that length of time. If the

yellow color disappears, a little more hydrogen peroxide is to be added.

The zirconia separates as a flocculent precipitate of basic zirconium phosphate,* which may easily be overlooked unless the flask is gently agitated. It is almost or entirely free from titanium, the precipitation of which is prevented by the addition of the hydrogen peroxide. However small the precipitate may appear, it is filtered off through a 5½-cm. filter, and well washed. For most rocks, in which the amount of ZrO_2 is very small, further purification is unnecessary, and the filter and precipitate are ignited in a small weighed crucible, and weighed as basic zirconium phosphate. This contains 51.8 per cent of ZrO_2, but for the minute quantities usually present it will suffice to multiply it by 0.5 to reduce it to ZrO_2. The percentage amount of ZrO_2 is to be subtracted from that of the ignited precipitate by ammonia to arrive at the correct figure for alumina.

If the precipitate is large, or if extreme accuracy is desired, the purification recommended by Hillebrand in every case may be carried out. The ignited precipitate (unweighed) is fused with a very little sodium carbonate, leached with water and filtered. The small filter and contents are ignited and then fused with a small lump of acid potassium sulphate, which is dissolved in hot water and a drop or two of dilute sulphuric acid. To the solution in the crucible a little hydrogen peroxide and a few drops of soluble phosphate are added, and the covered crucible is set aside as before. The precipitated zirconium phosphate now free from titanium, is collected, ignited and weighed as above. For identification of the zirconia the reader is referred to Hillebrand.

Baryta.—The residue left on solution of the zirconia in dilute sulphuric acid contains all the baryta, with traces of strontia and often much lime, as insoluble sulphates. To bring these into solution it is collected on a small filter, as described above, the filter and contents ignited in a small crucible and fused with about 1 gram of sodium carbonate, the fusion being continued

* Cf. P. E. Browning, Introduction to the Rarer Elements, 1903, p. 55.

for ten to fifteen minutes to permit the conversion of the barium sulphate into carbonate.

The cake is dissolved in warm water, which may be done in the crucible, filtered through a small filter, and well washed. After a fresh 250-c.c. beaker has been placed beneath the funnel, the carbonates are dissolved on the filter in a very little, warm, dilute hydrochloric acid, and the filter well washed. The liquid in the beaker is made up to at least 150 c.c., to prevent precipitation of the strontium and calcium sulphates, and 2 or 3 c.c. of concentrated sulphuric acid added. After standing for twenty-four hours, the precipitated barium sulphate is filtered off, ignited and weighed. It will seldom be necessary to purify it for contamination by calcium or strontium. Multiplication of the weight of $BaSO_4$ by 0.66 reduces it to BaO.

13. Sulphuric Anhydride.

This constituent, which occurs usually in the minerals haüyne and noselite, both soluble in hydrochloric acid, is determined in a separate portion. About 1 gram is weighed out (p. 144) into a 250-c.c. beaker, and gently boiled with 50 c.c. of dilute hydrochloric acid (1 : 5). If pyrite or pyrrhotite are present, a stream of carbon dioxide should be allowed to enter by the lip of the covered beaker, and to fill the space beneath the cover before boiling is begun. It is, of course, continued during the boiling. In this way any pyrite remains unattacked, while seven-eighths of the sulphur of pyrrhotite goes off as hydrogen sulphide, the remaining one-eighth being precipitated as sulphur. This need not be filtered off, as it is burned in the subsequent ignition.

After boiling for about a quarter of an hour, the liquid is filtered through a 9-cm. filter, and the residue and filter washed. The volume of liquid should be about 200 c.c., to prevent precipitation of silica. It is then precipitated, best while hot, with an excess of barium-chloride solution, allowed to stand for some time, the barium sulphate filtered off, well washed, ignited and weighed. To guard against contamination by silica it is always as well to evaporate the ignited precipitate with a few drops of

hydrofluoric and sulphuric acids, and reignite. The weight of $BaSO_4$ is multiplied by 0.343 to obtain that of SO_3.

It may be pointed out here that, before determining sulphur or sulphuric anhydride, the condition in which the sulphur exists in the rock should be investigated. The microscope will usually reveal the presence of pyrite or pyrrhotite, as well as noselite or haüyne. If not, the rock powder should be boiled with a little dilute hydrochloric acid, and if hydrogen sulphide is evolved the presence of pyrrhotite may be inferred, as the lazurite molecule is not apt to be found in rocks. A little of the filtered liquid may be tested with barium sulphate for SO_3. But whether a pyrite-like mineral is visible or not with the microscope, the determination of total sulphur should be made, if the rock is at all basic. It takes but little time or labor, and, as Hillebrand remarks, sulphur is to be found in nearly all rocks, sometimes in traces only, but again in quite appreciable quantities.

14. Chlorine.

While Hillebrand recommends fusion with chlorine-free sodium carbonate, to ensure getting all the chlorine, yet it is not only difficult to procure such a reagent, but the operation will be somewhat long and complex. For nearly all purposes simple solution in nitric acid, if desired with the addition of some hydrofluoric acid, will be quite sufficient.

About 1 gram of rock powder is weighed out into a 250-c.c. beaker and boiled with 50 c.c. of dilute nitric acid (1:5), which should have been previously tested as to freedom from chlorine, or a blank determination is to be made with the same volume of the acid to allow of a suitable correction if chlorine-free acid is unattainable. If the addition of hydrofluoric acid is desired the digestion should be carried out in a capacious crucible or small platinum basin.

After boiling for a quarter of an hour, the liquid is filtered,*

* A rubber or platinum funnel and the platinum basin are to be used if hydrofluoric acid has been added.

the filter and residue well washed and the filtrate precipitated with excess of silver nitrate solution. It is heated in a dim light, with constant stirring, to coagulate the silver chloride. If the precipitate is at all considerable, it is filtered through a small filter and, after washing, is dissolved on the filter with ammonia water, reprecipitated by acidifying with nitric acid to free it from possibly contaminating silica, and collected in a weighed Gooch crucible. After washing, it is dried, heated to incipient fusion and weighed. The weight of the AgCl multiplied by 0.247, or 0.25 for small amounts, will give the weight of chlorine present.

If the precipitate is very small, Hillebrand * recommends that it be collected on a small paper filter, which is then dried, wound up in a weighed platinum wire and carefully ignited. The increased weight of the wire is due to the metallic silver of the chloride which has alloyed with the platinum, and is multiplied by 0.33 to arrive at the chlorine.

If the chlorine is present only in minerals of the sodalite group, solution in nitric acid alone will usually be sufficient. But if scapolites are present, some of which are not attacked by this acid, the addition of hydrofluoric acid will be necessary.

In the determination of chlorine great care should be exercised that the reagents used are free from chlorine, and a duplicate operation in blank with the same quantities will always be a wise precaution. Rock specimens collected near the seashore are sometimes contaminated with sodium chloride derived from sea-water. This may be estimated in a separate portion by thorough washing on a filter with warm water, and determination of the chlorine dissolved out. This is, of course, to be deducted from the amount of chlorine which is found by the previous method, and its equivalent amount of Na_2O from that of this constituent already found.

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* Hillebrand, Bull. 176, p. 103; Bull. 305, p. 154.

15. FLUORINE.

To determine this constituent the method of Rose * may be followed, with modifications proposed by Penfield and Minor.† This may be described as follows:

About 2 grams of the rock powder are fused with five times its weight of alkali carbonates, and the cake thoroughly leached with hot water, filtered and washed. The filtrate contains all the fluorine as alkali fluorides. While still hot about 5 grams of ammonium carbonate are added to the filtrate, and when cold about the same amount is again added. The beaker is allowed to stand for about twelve hours, the precipitate filtered off and washed, and in the filtrate the ammonium carbonate is decomposed by heating on the water-bath till no more carbon dioxide is given off. About 5 c.c. of a solution of zinc oxide in strong ammonia water is added and the liquid evaporated till there is no more odor of ammonia. After filtering off the precipitate and washing, nitric acid is added to the filtrate till the alkali carbonate is nearly, but not entirely, decomposed. If too much is added, a solution of sodium carbonate is poured in to a decided alkaline reaction.

As chromic and phosphoric acids may be present, Hillebrand recommends the addition at this point of silver nitrate in excess, which will precipitate these substances. The liquid is heated and filtered, the excess of silver precipitated by sodium chloride, again heated to coagulation and again filtered, when a little sodium carbonate is added to alkaline reaction. If no chromium or phosphorus are present, or only small amounts, the addition of silver nitrate may be dispensed with.

The heated filtrate, which contains alkali carbonate and fluoride, and which must not contain ammonium salts, is now precipitated with an excess of calcium chloride. The precipitate of calcium carbonate and fluoride is collected on a filter, placed in

* Hillebrand, Bull. 176, p. 103; Bull. 305, p. 155.
† Penfield and Minor, Am. Jour. Sci., XLVII, p. 388, 1894.

a weighed platinum crucible, dried and ignited gently. A little water and 1 or 2 c.c. of acetic acid are poured in, and the covered crucible heated for some time on the water-bath, and finally the excess of acid evaporated with the cover off.

Hot water is poured on the dry salts, and the contents of the crucible are filtered through a small filter and washed. The filter with its contents are again ignited in the same crucible, and the digestion with dilute acetic acid and evaporation gone through with again. The ignition of the filters and the digestion with dilute acetic acid are repeated till all the calcium carbonate and oxide are dissolved as acetate, as shown by the evaporation of a few drops of the filtrate on platinum foil.*

The filter and purified calcium fluoride are finally gently ignited in the crucible and weighed. Multiplication of the weight of CaF_2 by 0.49, or division by 2 in most cases, gives the amount of fluorine. For possible corrections see Hillebrand.

A colorimetric method of determining the small amounts of fluorine found in rocks, based on the bleaching effect of fluorine on hydrogen peroxide solutions of titanium, has been proposed by G. Steiger.† The method consists in brief in fusing the rock with sodium carbonate, leaching with water, and mixing a definite amount of standard titanium soloution with the filtrate, which is compared colorimetrically with a fluorine-free titanium solution. The percentage of fluorine is shown by reference to a curve which has been determined empirically, and for this and other details the student must be referred to the original paper. The method may be recommended for use in rock analysis for its rapidity, simplicity, and probably greater accuracy than the usual gravimetric methods.

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* Penfield and Minor show that the addition of acetic acid in large amount leads to loss of calcium fluoride.

† Jour. Amer. Chem. Soc., XXX, 219, 1908.

16. Carbon Dioxide.

As all the minerals which contain this constituent are soluble in hydrochloric or nitric acid with evolution of CO_2 (dolomite and siderite only on warming), its qualitative presence may be easily established by warming the rock powder with a little, somewhat dilute nitric or hydrochloric acid, and noting whether effervescence ensues. This is best done in a test tube. If there is no marked effervescence, one may make sure of the reaction, as Hillebrand* suggests, by inclining the tube and examining the upper side with a lens for the stream of minute bubbles. Before the addition of the acid the powder should be well stirred up with warm water to drive out any mechanically attached air, bubbles of which might be mistaken for CO_2. If the rock contains considerable pyrrhotite, the evolution of H_2S may be mistaken for that of CO_2, but the former is easily recognizable by its characteristic odor, as well as by the blackening of paper soaked in lead acetate solution to which a little ammonia has been added.

The determination of carbon dioxide is effected by the usual method, which is so well known that a brief description will suffice. Any of the well-known forms of apparatus may be used, and if many determinations are to be made it will be as well to have one permanently set up.

At least 2 or 3 grams of rock powder are weighed out into a small flask. After mixing the powder with some water, the flask is connected on one side with a cylinder filled with soda-lime or sticks of caustic alkali, and a wash-bottle or two containing sulphuric acid, to dry the air and free it from CO_2. On the other side it is connected with an upward inclined condenser, or a tall cylinder filled with calcium chloride, then a U-tube filled with calcium chloride and one filled with pieces of pumice soaked in copper-sulphate solution and heated till the salt becomes anhydrous. This last is to retain any H_2S or HCl which may escape from the flask. The weighed U-tube for the absorption of the CO_2 follows these, and is protected on the

* Hillebrand, Bull. 305, p. 150.

other side from the moist air of the aspirator by a U-tube containing in one arm calcium chloride and in the other soda-lime.

After weighing the soda-lime U-tube and connecting it in place, the whole apparatus is filled with dry and carbon-dioxide-free air by means of an aspirator attached to the last U-tube. About 10 c.c. of dilute hydrochloric acid are added to the flask containing the powder and its contents boiled gently while a slow current of CO_2-free air is passing. In ten or fifteen minutes decomposition is complete, when the flame is removed and the current of air is continued for some time longer, till all that in the flask and tubes has been replaced.

The U-tube is then removed, carefully closed, and allowed to cool thoroughly, as the absorption of the CO_2 by the soda-lime gives rise to considerable heat. It is then weighed, the increase being the amount of CO_2 in the portion of rock powder taken.

A very simple and sufficiently accurate apparatus for the indirect determination of CO_2 by loss of weight has been described by Kreider.*

17. Chromium and Vanadium.

These constituents are so seldom present in appreciable amount in silicate igneous rocks that the analyst will not often be called on to determine them. The determination of vanadium, especially, is so seldom necessary, and the method so complex, that it need not be given here. If it is desired to determine it, Hillebrand's method should be used, a full description of which is given by him.†

Chromium is occasionally to be determined in such rocks as dunites, peridotites, pyroxenites, etc., and for this the colorimetric method recommended by Hillebrand ‡ is to be used. It is briefly summarized here.

* Amer. Jour. Sci., XIX, p. 188, 1905; cf. Hillebrand, Bull. 305, p. 152.
† Hillebrand, Bull. 176, p. 82; Bull. 305, p. 127.
‡ Hillebrand, Bull. 176, p. 80; Bull. 305, p. 124.

At least a gram of rock powder is thoroughly fused with sodium carbonate, to which a little nitre is added, and the cake extracted with water, as in the method for total sulphur (p. 170). A few drops of either ethyl or methyl alcohol are added to destroy the color of sodium manganate, and the liquid is filtered. If the yellow color is very faint, or invisible, the liquid should be concentrated to small bulk for use as the test solution, and placed in a small measuring-flask of 25, 50 or 100 c.c., according to the depth of color, which must be less than that of the standard solution. This last is prepared by dissolving 0.25525 gram of normal potassium chromate (K_2CrO_4) in a liter of water, the solution containing then 0.0001 gram of Cr_2O_3 per cubic centimeter.

The depth of color of the test solution is then compared with that of the standard exactly as was done in the determination of titanium dioxide (p. 118) by the colorimetric method, a definite volume of standard being diluted with water from a burette till the two colors are alike. The results, as shown by Hillebrand, are very accurate for the small quantities found in rocks.

18. Copper and nickel.

If it is desired to determine copper. or other metals of the hydrogen-sulphide group, which may rarely be present, it is advisable to use a separate portion, rather than determine them in the sulphides remaining after determination of manganese in the main portion, if the acetate method has been used. This is chiefly because in this they are contaminated with platinum, and partly because appreciable amounts of copper will probably have been introduced from the water-baths (Hillebrand).

The weighed portion, preferably of 2 grams, may be decomposed by sulphuric and hydrofluoric acids, and repeated evaporations with additions of the former to drive off all traces of the latter. Or, as seems preferable to me, the solution is effected by a mixture of nitric and hydrofluoric acids, filtration in a rubber

funnel, and evaporation of the filtrate in a small porcelain basin (a platinum basin should not be used). Thus far the operation is identical with that for the determination of phosphoric anhydride (p. 163).

After heating the dried salts in the basin to drive off excess of acid and render the silica insoluble, they are dissolved in 25 c.c. of dilute hydrochloric acid, filtered, and the diluted filtrate precipitated by a current of H_2S. The precipitated cupric sulphide is filtered off rapidly and washed with water containing H_2S. The filter containing it is ignited in a small weighed platinum crucible, moistened with a few drops of nitric acid, cautiously evaporated to dryness, ignited, and the residue weighed as CuO. Multiplication of this by 0.8 reduces it to Cu.

Ammonia in excess is added to the filtrate, and a current of H_2S passed through it for a quarter of an hour, a few drops of acetic acid are added, and the liquid allowed to stand for some hours, when the nickel (and cobalt) sulphides are caught on a 5½-cm. filter, ignited and weighed as oxide. The amount of cobalt in terrestrial rocks is so small that it is not necessary to separate it from the nickel, but its presence may be established, if desired, by testing the oxide with the borax bead.

APPENDIX.

1. Example of Analysis.

In order to render perfectly clear the method of recording the results, and of carrying out the various calculations, an example is given of an actual analysis. That chosen is one which was made by me for the Carnegie Institution, and I desire to express my thanks to the Trustees for their permission to make use of it here. Some of the minor constituents which were determined are not given in this place. For recording an analysis the student should select a note-book with a sufficiently large page, and, in the following example, the different pages are indicated by the horizontal lines.

1310. LEUCITE-TEPHRITE, LAVA OF 1903, MT. VESUVIUS.

Cruc. + subst. = 40.6602
Cruc. = 39.6562

Subst. taken = 1.0040

SiO_2 48.10

Cruc. + SiO_2 + x = 33.1879
Cruc. = 32.7043

.4836

Cruc. + SiO_2 + x = 33.1879
Cruc. + x = 32.7078

SiO_2 = .4801
Extra SiO_2 = .0028

1.004) .4829 (.48098
4016

8130
8032

9800
9036

7640

H_2O- 0.04

Cruc. + subst. = 34.9497
Cruc. = 33.8717

1.0780

Cruc. + subst. = 34.9497
Dried at 110° = 34.9493

.0004

H_2O+ 0.11

Tube + subst. = 25.3857
Tube = 24.2037

1.1820

Total H_2O = 0.15
H_2O- = 0.04

H_2O+ = 0.11

Tube + H_2O = 20.7298
Tube − H_2O = 20.7280

1.18) .00180 (.0015
118

620
590

300

1310. Al_2O_3, Fe_2O_3, P_2O_5.

Cruc. + Al_2O_3, etc. = 33.0007 — Cruc. + res. + SiO_2 = 33.8747
Cruc. = 32.7043 — Cruc. + res. − SiO_2 = 33.8719
.2964 — Extra SiO_2 = .0028

Used 36.6 c.c. of permanganate sol.

Al_2O_3 17.59

Al_2O_3, etc. = .2964
Fe_2O_3 = .0930
.2034

Fe_2O_3 2.48

SiO_2 = .0028
.2006
P_2O_5 = .0098
.1908
TiO_2 = .0142

1.004).1766(.1759
1004
7620
7028
5920
5020
9000

.002541
36.6
15246
15246
7623

Total Fe_2O_3 = .0930006
FeO as Fe_2O_3 = .0680712

1.004).0249294(.0248
2008
4849
4016
8330

Pt basin + subst. = 11.1134 — Cruc. + $Mg_2P_2O_7$ = 19.0322
Pt basin = 10.0830 — Cruc. = 19.0165
1.0304 — .0157

P_2O_5 0.98

1.004
.0098
8032
9036
.0098392

.64
628
942
1.0304).0100480(.00975
92736
77440
72128
53120

CO_2 none

No CO_2

1310. FeO, TiO_2.

FeO 6.10

Cruc. + subst. = 35.9546
Cruc. = 35.4488

.5058 = 13.5 c.c. of $K_2Mn_2O_8$

.002287	.002541	1.004
13.5	13.5	.0678
11435	12705	8032
6861	7623	7028
2287	2541	6024
.5058).0308745(.06104	.5058).0343035(.0678 =	.0680712
30348	30348 FeO as Fe_2O_3	
5265	39555	
5058	35406	
20700	41490	
	40464	
	10260	

TiO_2 1.41

Test solution diluted to 500 c.c.

Dilute $(\frac{1}{10})$ standard = 10 c.c. + 25.0 c.c. H_2O
" $(\frac{1}{10})$ " = 10 c.c. + 25.3 " "
" $(\frac{1}{10})$ " = 10 c.c. + 25.5 " "
3)75.8 c.c. H_2O

10 + 25.267 = 35.267 c.c.

35.267).001000000(.00002836	.00002836
70534	500
294660	00.01418000
282136	
125240	1.004).01418(.0141
105801	1004
194390	4140
	4016
	1240

1310. CaO, MgO.*

CaO 8.16

Cruc. + CaO = 33.9533
Cruc. = 33.8714

.0819

1.004).08190(.0816
8032

1580
1004

5760

MgO 4.27

Gooch cruc. + $Mg_2P_2O_7$ = 25.1389
Gooch cruc. = 25.0205

.1184

.1184
.3621

1184
2368
7104
3552

1.004).4287264(.0427
4016

2712
2008

7046

* On this page are also recorded the figures for S, ZrO_2, and BaO, which are omitted here.

1310. Alkalies.*

Tube + subst. = 23.5598
Tube − subst. = 23.0263

.5335

Cruc. + NaCl + KCl = 35.5417
Cruc. = 35.4481

.0936

Gooch cruc. + K_2PtCl_6 = 25.2593
Gooch cruc. = 25.0410

.2183

K_2O 7.93

.2183
.1939

19647
6549
19647
2183

Na_2O 2.65

.5335).04232837(.07934
37345

49833
48015

18187
16005

21820

.2183
.307

15281
65490

.0670181 (= KCl)

.0936
.0670

.0266
.5308

2128
7980
1330

.5335).01411928(.0265
10670

34492
32010

24828

* No correction was needed for the amount of alkalies in the calcium carbonate used.

2. Table of Molecular Weights.

SiO_2	60	ZrO_2	123
Al_2O_3	102	P_2O_5	142
Fe_2O_3	160	SO_3	80
FeO	72	Cl	35.5
MgO	40	F	19
CaO	56	S	32
Na_2O	62	Cr_2O_3	152
K_2O	94	MnO	71
H_2O	18	NiO	75
CO_2	44	BaO	153.5
TiO_2	80	SrO	103.5

These molecular weights are the approximate ones which are generally employed in petrographical calculations.

3. Factors for Calculation.

Constituent	Sought	Found	Factor
Baryta	BaO	$BaSO_4$	.66
Chlorine	Cl	$AgCl$	.247
Chlorine	Cl	Ag	.33
Copper	Cu	CuO	.80
Fluorine	F	CaF_2	.49
Magnesia	MgO	$Mg_2P_2O_7$	.3627
Manganous oxide	MnO	Mn_3O_4	.93
Phosphoric anhydride	P_2O_5	$Mg_2P_2O_7$	.637
Phosphoric anhydride	P_2O_5	$24MoO_3.P_2O_5$	.04
Potash	K_2O	K_2PtCl_6	.1939
Potash	KCl	K_2PtCl_6	.3070
Soda	Na_2O	$NaCl$	.5308
Strontia	SrO	$SrSO_4$	.56
Sulphur	S	$BaSO_4$	.137
Sulphuric anhydride	SO_3	$BaSO_4$	.343
Zirconia	ZrO_2	$xZrO_2.yP_2O_5$	.52

These factors are only carried out as far as is deemed appropriate for the quantities usually found in igneous rocks.

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